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Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN COLORED SUBSTANCES DERIVED FROM NITRO COMPOUNDS.[1]

[FOURTH PAPER.]

BY C. LORING JACKSON AND R. B. EARLE.

The colored addition-compounds obtained from nitro derivatives of benzol and sodic alcoholates, or other alkaline bodies, have been the subject of frequent study. For an account of this work the reader is referred to the previous papers from this laboratory.[2]

In these papers will be found convincing arguments against Victor Meyer's theory that these compounds are formed by the replacement by a metal of an atom of hydrogen attached to the benzol ring. In a paper from the laboratory at Marburg, published in 1899, Drost[3] describes some salts of the metadinitroorthodinitrosobenzol, and gives analyses which seem to indicate that they were formed by the replacement of 1 atom of hydrogen by 1 of the metals. As in this way he

[1] The work described in this paper formed part of a thesis presented to the faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science by R. B. Earle.

[2] Jackson and Ittner: This JOURNAL, 19, 199; Jackson and Boos: *Ibid.*, 20, 444; Jackson and Gazzolo: *Ibid.*, 23, 376.

[3] Ann. Chem. (Liebig), 307, 49.

revives the theory of Victor Meyer, it is necessary to discuss his work in detail. His salts were formed by the action of an alkaline carbonate or hydrate on the dinitrodinitrosobenzol; if then they belong to the same class as the other salts from nitrobenzol derivatives, which seems probable from their properties, they should be formed by the addition of the metal and hydroxyl to the mother substance. This view of their composition was overlooked at first by Drost and Zincke,[1] as neither of them seemed to be aware of the work on this subject by Lobry de Bruyn,[2] and that from this laboratory,[3] which is not surprising, as it is almost impossible to look up the literature of a subject like this, which cannot be indexed under the names of definite compounds. In a later paper[4] Drost discusses these addition formulas, to which his attention was called by Hantzsch and Kissel's paper[5] (considered later), but rejects them on the ground of his analyses, especially that of the ammonium salt, and also because the compounds are formed from primary and secondary carbonates, which compels the assumption that the nitro compounds in aqueous solutions can behave as nitro acids, or that there is a hydrolytic decomposition of the carbonates. It seems to us that neither of these assumptions offers greater difficulties than the one made by Drost, that the hydrogen in the dinitrodinitrosobenzol is so loosely attached as to make it possible for this substance to decompose a carbonate in aqueous solution at 60° to 70°. Having disposed of this minor objection, the adoption of Drost's formulas rests on his analytical results, as should be the case. Accordingly, we compare below the percentages calculated by Drost for the salts, if formed by replacement of hydrogen with the metal, Drost's analytical results, and the percentages calculated if the salt was formed according to our view by the addition of metal and hydroxyl:

[1] Zincke and Schwartz: Ann. Chem. (Liebig), **307**, 32 (1899). Zincke's hypothesis of the formation of an unstable phenol, $C_6HNO_2(NO)_2OH$, in order to explain Drost's salts is unnecessary, if the salts prove to be addition- instead of substitution-compounds.

[2] Rec. trav. chim. Pays-Bas, **14**, 89.

[3] This JOURNAL, **19**, 203; **20**, 444; **23**, 376.

[4] Ann. Chem. (Liebig), **313**, 299 (1900).

[5] Ber. d. chem. Ges., **32**, 3137 (1899).

	Calculated for $C_6HN_4O_6K + \frac{1}{2}H_2O$. Drost's formula.	Calculated for $C_6H_2N_4O_6OHK$. Our formula.	Found. Drost.
C	26.34	25.52	26.33
K	14.32	13.87	14.13

	Calculated for $C_6HN_4O_6Ag$.	Calculated for $C_6H_2N_4O_6OHAg$.	Found.
Ag	32.40	30.77	30.65

	Calculated for $C_6HN_4O_6NH_4$.	Calculated for $C_6H_2N_4O_6OHNH_4$.	Found.
N	28.86	26.82	28.94

It appears from this comparison that the theory of Drost is supported by the nitrogen determination in the ammonium salt, but is not in harmony with the percentage of silver in the silver salt, and is only brought into close agreement with the percentages of potassium and carbon found by assuming that the potassium salt contains 0.5 molecule of water. The anhydrous salt would contain 27.26 per cent of carbon and 14.80 per cent of potassium. On the other hand, our theory is in agreement with the potassium, and silver might pass for the carbon, although it is not so good as Drost's, since it is below the percentage found, and does not agree with the nitrogen determination in the ammonium salt. The analytical results, therefore, are not incompatible with our formulas, especially when it is borne in mind that the silver salt, formed by precipitation, would probably be the purest of the salts analyzed, whereas the ammonium salt (which does not agree with our formula) had a brownish color, which may indicate decomposition. In the present condition of the subject we cannot accept Drost's analytical results as re-establishing Victor Meyer's theory that these salts are formed by the substitution of an atom of metal for an atom of hydrogen attached to the benzol ring. We hope that he will return to the subject and provide analytical material sufficient to decide finally between the two formulas, especially as he states that he does not consider his present data adequate.

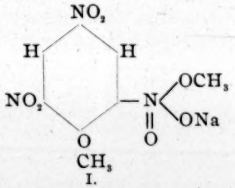
The important paper of Hantzsch and Kissel,[1] although published before the paper by Gazzolo and one of us,[2] arrived

[1] Ber. d. chem. Ges., **32**, 3137.
[2] This JOURNAL, **23**, 376.

too late for proper discussion in it. They prepared the addition-compound from symmetrical trinitrotoluol and potassic methylate and succeeded in isolating from it the free acid, while all attempts to prepare the free acid from the corresponding benzol or xylol derivative failed.

By treating the free acid with acetyl chloride the acetyl derivative was obtained, which, as they point out, proves that these are true compounds instead of containing alcohol of crystallization according to Victor Meyer's theory. This point was also proved by determinations of molecular weight and electrical conductivity with some of these compounds.

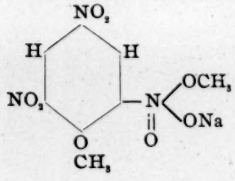
In discussing the structure of these salts they pronounce in favor of the nitroester acid formula, I.,[1] but give no arguments



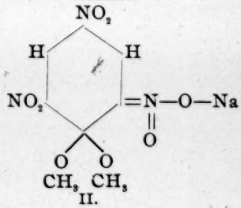
I.

to prove its superiority to the quinoid formula, which apparently had not occurred to them as a possibility.[2]

In the paper by Gazzolo and one of us,[3] the formula I. and the quinoid formulas II. or III. were discussed and the preference given to the latter.



I.

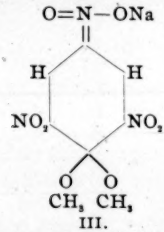


II.

[1] All formulas in the discussion are those of the product from trinitroanisol and sodic methylate.

[2] Their paper led Angeli (Atti R. Accad. Lincei, [5], **9**, I., 41), to recall the fact that in 1897 (Gazz. chim. ital., **27**, II., 357) he was of the opinion that these substances were addition-compounds.

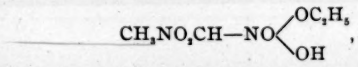
[3] This JOURNAL, **23**, 381.



III.

The arguments which led us to this conclusion will be given briefly as an introduction to the discussion based on more recent experimental data. Formula II. or III. is more in harmony with the following properties of the substance than formula I. is,—the strong color, the instability of the free acid, and the substitution of both methyl radicals by benzyl when the compound is allowed to stand with benzyl alcohol. For the full statement of these arguments the reader is referred to the paper[1] by Gazzolo and one of us, already cited.

Hantzsch and Kissel in their paper[2] furnish another strong argument in favor of formula II. or III., as they state that the free acid obtained by them, $C_6CH_3H_2(NO_2)_3HOCH_3$, is a weak acid, whereas, if it were a nitroester acid, it should be a very strong one, since Hantzsch and Rinckenberger[3] found that the analogous acid,



is ten times as strong as acetic acid. This fact they could not explain by formula I., but it at once becomes intelligible with formula II. or III., which puts the two acids in different classes. The strong color of the compounds also puzzled Hantzsch and Kissel, but is explained by the quinoid formulas.

[1] This JOURNAL, **23**, 381.

[2] Ber. d. chem. Ges., **32**, 3137.

[3] *Ibid.*, **32**, 628. In this paper the nitroester acid theory for these compounds is proposed.

The last paper[1] on this subject is one by Meisenheimer, which reached us while we were preparing this manuscript for the press. He overlooked the paper by Jackson and Gazzolo[2] just cited, which is the more strange because he quotes the preceding paper[3] of this series. This oversight has led him to publish as original the quinoid theory of these compounds, although a complete discussion of it had appeared in that paper two years earlier, including all the arguments from the properties of the bodies given by him. To these he adds a proof of the quinoid theory similar to that given in this paper. This unnecessary duplication of work is certainly to be regretted. In his experimental work he has failed to meet a serious objection to his proof, which it will be more convenient to discuss later in connection with the account of our own work.

The arguments from the properties of these bodies given above, while they create a strong presumption in favor of formula II. or III., do not constitute a final proof of this structure. We accordingly tried to furnish a more convincing argument, and after spending much time in applying, without success, reactions to these substances which would show their affinity to quinones,[4] we at last hit upon an experiment which seems to us conclusive in favor of formula II. or III. This experiment consisted in preparing and analyzing an addition-compound containing two different alkyl radicals and studying the products of its decomposition with hydrochloric acid. As it was necessary that the two radicals should be as different as possible, so as to make the analytical results decisive, we tried first the addition of sodic benzylate to trinitroanisol, but, as this proved unmanageable, we substituted sodic isoamylate for sodic benzylate, and with this obtained a compound, $C_6H_3(NO_2)_3OCH_3NaOC_5H_{11}$, the composition of which was established by three sodium determinations and a combustion. It was necessary for our purpose to prove that this substance was a chemical individual, and the analyses did not

[1] Ann. Chem. (Liebig), **323**, 205.

[2] This JOURNAL, **23**, 376.

[3] Jackson and Boos: *Ibid*., **20**, 444.

[4] A brief account of these experiments will be found in the experimental part of this paper.

do this, since the following reactions might have taken place:

I. $C_6H_2(NO_2)_3OCH_3 + NaOC_5H_{11} = C_6H_2(NO_2)_3OC_5H_{11} + NaOCH_3$;

II. $C_6H_2(NO_2)_3OCH_3 + NaOCH_3 = C_6H_2(NO_2)_3OCH_3.NaOCH_3$;

III. $C_6H_2(NO_2)_3OC_5H_{11} + NaOC_5H_{11} = C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$;

which would give as the product a mixture in molecular proportions of the dimethyl and the diisoamyl addition-compounds. This mixture would give the same results on analysis as the compound $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$. The chances that it was such a mixture were not very great, as the product dissolved to a certain extent in the benzol used as a precipitant in making it, and therefore we could have got our concordant analytical results from a mixture only in case its two components dissolved to exactly the same extent in benzol, which was far from probable; but as our proof of the quinoid theory depended on the individuality of this product, we felt it necessary to prove absolutely that it was a single compound and not a mixture, and this we did by determining its solubility and comparing it with those of its possible components, for, although it is decomposed in time by water, it can exist in an ice-cold solution for a long enough time to carry out this determination. The solubilities found were as follows:

100 parts of the solutions at 0° contain the following amounts of the solids:

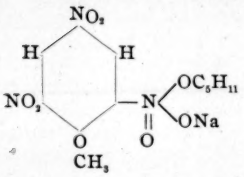
$C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$	1.508	1.110
$C_6H_2(NO_2)_3OCH_3.NaOCH_3$	0.4751	0.6412
$C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$	0.0960	0.0921

The conditions as to time occupied and mode of treatment were as nearly identical as possible in all the determinations. The want of close agreement in the results shows that the solutions underwent some decomposition during the experiments, but this is not sufficient to render them useless for our purpose, as the difference between the lowest solubility of our substance, $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$, and the sum of the

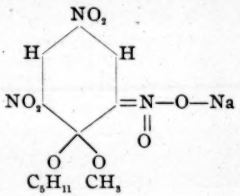
highest determinations of its two components, if it were a mixture, is 0.3728, whereas the largest experimental error, that in the methylate compound, is 0.1661, so that there can be no doubt that our substance is a compound and not a mixture of constant composition.

The compound having been characterized in the way just given, it was next decomposed by treating a benzol solution of it with dilute hydrochloric acid. The product of this reaction began to melt at 62°, but did not become entirely liquid until 69°. From it we isolated isoamyl picrate, which was recognized by its melting-point, 68° to 69°, and by an analysis. That the other product of the reaction was trinitroanisol was proved by the fact that the presence of methoxyl was shown in it by the method of Zeisel, taken in connection with the melting-point of the crude product, 62° to 69° (trinitroanisol melts at 64°). This determination by the method of Zeisel also gave the amount of trinitroanisol present in the mixture. We found it to be 45.25 and 45.94 per cent. The percentage calculated, if the mixture consisted of trinitroanisol and isoamyl picrate in molecular proportions, is 44.83. The agreement is as near as could be expected. A rough method of determining the amount of isoamyl picrate was also tried, consisting in decomposing the mixture with potassic hydrate, extracting the amyl alcohol with chloroform, and weighing the dried amyl alcohol (which showed the proper boiling-point 131°); this gave 48 per cent of isoamyl picrate against 55.17 per cent calculated for a mixture in molecular proportions. The agreement is as close as could be expected considering the unavoidable losses entailed by the manipulations.

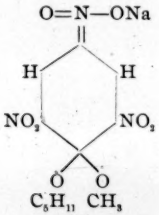
The result of the experiment, then, is that the compound $C_6H_3(NO_2)_3OCH_3.NaOC_5H_{11}$, when decomposed by hydrochloric acid, yields a mixture of trinitroanisol and isoamyl picrate in nearly molecular proportions. The formulas of the compound according to Hantzsch and Kissel's theory is given under IV., according to our theory under V. or VI.



IV.



V.



VI.

The explanation of the formation of isoamyl picrate from a substance with formula IV. necessitates a series of strained, improbable, molecular transformations, whereas the formation of equal molecules of trinitroanisol and isoamyl picrate by the decomposition of a body constituted as in formula V. or VI. is what would naturally occur by the splitting off of isoamyl alcohol from some molecules and methyl alcohol from others. This experiment, therefore, seems to give decisive evidence in favor of the quinoid theory.

It might be objected to the foregoing proof that perhaps the isoamyl picrate was not formed from the addition-compound, but was a result of the action of isoamyl alcohol on the trinitroanisol after it had been set free. This was met by an experiment which showed that isoamyl alcohol had no action on trinitroanisol.

As has been stated already, this proof was anticipated by Meisenheimer,[1] who studied the addition-products made from

[1] Ann. Chem. (Liebig), 323, 242.

trinitroanisol and potassic ethylate, and from trinitrophenetol and potassic methylate. The composition of each substance was determined by complete analyses, and, after decomposition with sulphuric acid, ethyl picrate was isolated in each case. Similar results were obtained from the addition-compounds of trinitroanisol with potassic isobutylate, and isobutyl picrate with potassic methylate. The objection that these substances might be mixtures of

$$C_6H_2(NO_2)_3OCH_3.KOCH_3 \text{ and } C_6H_2(NO_2)_3OC_2H_5.KO.C_2H_5$$

in molecular proportions was not met by Meisenheimer. Such a mixture might be formed by reactions similar to those given in the discussion of our work, or in another way peculiar to the experimental conditions used by Meisenheimer, since he made his addition-compound from trinitroanisol in ethyl alcohol solution, and it has been shown[1] repeatedly that one of these addition-compounds in contact with another alcohol is converted into the corresponding derivative of this alcohol. The ethyl alcohol therefore might well have formed enough of the ethyl compound to make the mixture. In fact it is strange that he obtained the methyl-ethyl rather than the diethyl compound. The explanation is probably to be found in the low temperature used by him.

The only marked difference between Meisenheimer's results and ours lies in the relative proportions of the two products. He thinks that more than 50 per cent of the picrate of the heavier alkyl radical is formed in every case, whereas our rough quantitative determinations pointed to a mixture of equal molecules. The cause of this discrepancy is probably to be found in the method of acidification or of purification of the product. Meisenheimer shook the salt with water and ether after acidifying with sulphuric acid. The ethereal solution of the decomposition-products was washed with sodic carbonate solution until it was almost colorless. The aqueous solution was colored dark reddish-brown. In our work the

[1] Jackson and Boos: This JOURNAL, **20**, 449; $C_6H_2(NO_2)_3OCH_3.NaOCH_3 + 2C_2H_5OH = C_6H_2(NO_2)_3OC_2H_5.NaOC_2H_5 + 2CH_3OH$; Jackson and Gazzolo: This JOURNAL, **23**, 394. Similar reactions with benzyl alcohol on the dimethyl compound, and methyl alcohol on the dibenzyl compound. These results are confirmed by the action of isoamyl alcohol on the dimethyl compound described later in this paper.

salt was suspended in benzol and shaken with dilute hydrochloric acid, the benzol solution washed with water, which showed no color, and the slightly yellow residue, after the benzol had been evaporated, washed with about 2 cc. of cold alcohol. The strong color in Meisenheimer's experiments certainly indicates a secondary reaction, perhaps autoxidation,[1] by which more trinitroanisol than trinitrophenetol may have been decomposed. On the other hand, the only chance for loss in our work lay in the washing with alcohol, but, as this removed only about 4 per cent of the total product (0.13 gram from 3 grams), it could not have had an appreciable influence on the proportions found by us. We feel constrained, therefore, to uphold our results against Meisenheimer's until the point is definitely settled by further experiments.

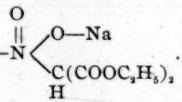
Meisenheimer suggests the name quinolnitro acids for these substances, which we adopt, as it seems to us better than the one we had invented. We have, however, in the experimental part of this paper named the salts after their components, adding the new names in parentheses, as we think this arrangement will be easier for the reader.

In our attempts to get characteristic quinone reactions from these bodies, the observation was made that when the addition-compound of trinitroanisol and sodic methylate (sodium salt of dinitrodimethoxyquinolnitro acid) was treated with aniline or hydroxylamine, both the methoxyl groups were driven out. This observation is in harmony with the quinoid theory, but, if the substance is a nitroester acid, there is no reason why more than one methoxyl should be displaced, since stable addition-products have been obtained from aromatic nitro bodies containing the anilido group. While this reaction yielded too indefinite aromatic products to be used as a proof of the quinoid theory, it seems to us to furnish a confirmatory argument in favor of it.

The only serious objection to the quinoid theory, which we have found, lies in the fact that the sodic malonic ester (or acetoacetic ester) compound derived from trinitroanisol is decomposed by acids with the utmost ease, with regeneration of

[1] Compare our study of the decomposition of the trinitrobenzoldimethylate described later in this paper.

trinitroanisol. If the sodic malonic ester splits into sodium and $-CH(COOC_2H_5)_2$, in order to make the addition, this, according to the quinoid theory, would give a union of the carbon of $-CH(COOC_2H_5)_2$ with the carbon of the benzol ring, which would be too stable to be broken up at once by dilute hydrochloric acid. The same difficulty, however, applies to Hantzsch and Kissel's nitroester theory, as in this case the carbon of the $-CH(COOC_2H_5)_2$ would form a stable union with the nitrogen of the nitro group, thus:



The difficulty can be removed in both cases by supposing the malonic ester residue is added in its tautomeric enol form; thus, $-O-C(OC_2H_5)=CH-COOC_2H_5$, when the less stable attachment of oxygen to carbon (or nitrogen) would be formed. This subject seems to us worthy of further study.

In considering the formation of both trinitroanisol and isoamyl picrate from the compound $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$ by acids it seemed probable to us that the relative amounts of the two products formed might depend on the amount of one or the other free alcohol present. In that case a decomposition carried on in the presence of an excess of methyl alcohol should consist principally in the removal of isoamyl alcohol, and should therefore give a larger proportion of the trinitroanisol than when the acidification took place only in benzol. An experiment showed, however, that a large excess of methyl alcohol had no effect whatever, no more trinitroanisol being formed in this case than when the decomposition took place in benzol alone.

It has been proved[1] that if the sodium salt of dinitrodimethoxyquinolnitro acid is boiled with ethyl alcohol the product, on decomposition with hydrochloric acid, yields ethyl picrate; also that the same salt, if soaked in benzyl alcohol, yields with an acid benzyl picrate,[2] or, if the dibenzyl salt is

[1] Jackson and Boos; This JOURNAL, **20**, 449.

[2] Jackson and Gazzolo: *Ibid.*, **23**, 394.

boiled with methyl alcohol, trinitroanisol is obtained on acidification ; but the only analysis of the salt of the new quinolnitro acid formed by the action of an alcohol was one of the diethyl compound formed by boiling the dimethyl body with ethyl alcohol, in which the difference in the percentages of sodium was too small to give conclusive results. It seemed of interest, therefore, to analyze a product where the difference in the size of the alkyl radicals would make the analytical results of some value. Accordingly, we treated the dimethyl compound with isoamyl alcohol at 70° for ten minutes, and found, by analysis of the product, that the following reaction had taken place :

$$C_6H_2(NO_2)_3OCH_3.NaOCH_3 + 2C_5H_{11}OH = 2CH_3OH + C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}.$$

Delepine[1] has shown that an acetal boiled with a different alcohol and 1 to 3 drops of hydrochloric acid is in a short time converted into the acetal of the alcohol used. This reaction, therefore, is entirely in harmony with the quinoid acetal formula, but it seems hard to find a reason why the methoxyl attached to the ring (the anisol methoxyl) should be replaced by isoamyl alcohol, if the addition-compound is a nitroester acid, according to Hantzsch and Kissel, in view of the fact that trinitroanisol is entirely unaffected by isoamyl alcohol at 100°. This argument for the quinoid theory was given in the paper by Gazzolo and one of us, but in a less exact form.

The experimental material at present collected is not sufficient to make it possible to decide whether these substances are ortho or paraquinoids. We hope that the work of the coming year in this laboratory will provide material for at least a partial solution of this problem.

The paper by Gazzolo and one of us contained descriptions of addition-compounds formed with sodic malonic-ester, sodic acetoacetic ester, or sodic isoamylate, which contained 3 molecules of the alkaline substance to each molecule of the trinitro compound (trinitrobenzol or trinitroanisol), whereas all the addition-compounds previously analyzed contained only 1 molecule of the alkaline substance. In that paper addition-com-

[1] Compt. rend., 132, 968.

pounds of sodic ethylate or methylate with trinitrobenzol were mentioned, which seemed to contain more than 1 molecule of alcoholate, but the formulas for which could not be established by the sodium determinations then alone at our disposal. On returning to this subject, we soon found that the samples analyzed by Gazzolo had been decomposed, as the substance does not keep even *in vacuo*. We accordingly prepared and dried samples of the methyl compound with as little delay as possible, and found it was formed by the addition of 2 molecules of sodic methylate to one of the trinitrobenzol, thus: $C_6H_3(NO_2)_3(NaOCH_3)_2$. The spontaneous decomposition of this substance seems to consist in at least two parallel reactions. In one, methyl groups are oxidized to formaldehyde by the oxygen of a nitro group, forming the tetranitroazoxybenzol, $(C_6H_3(NO_2)_2)_2N_2O$, melting at 183°, that was discovered by Lobry de Bruyn.[1] The second reaction, which was made out with less certainty, seemed to consist in the formation of sodic nitrite and a nitrophenol.

This substance, $C_6H_3(NO_2)_3(CH_3ONa)_2$, is of interest, as it is the first which contains 2 molecules of an alcoholate. It was formed even in the presence of a large excess (4 molecules) of the sodic methylate, and none of our attempts to prepare a methylate addition-compound containing more than 2 molecules of sodic methylate have been successful. In our work we have succeeded in analyzing also the following addition-compounds containing 2 molecules of the alkaline material:

$$C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2;$$
$$C_6H_3(NO_2)_3(NaOC_6H_5)_2;$$
$$C_6H_2(NO_2)_3OCH_3(KCN)_2.$$

Of these, the first is the most interesting in this connection, because the mono compound, $C_6H_2(NO_2)_3OCH_3.NaOCH_3$,[2] is also known. This compound, with 1 molecule of methylate, is a bright-red, crystalline substance of great stability for a substance of this class, remaining unaltered even when exposed to the air for a long time. The compound

$$C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2,$$

[1] Rec. trav. chim. Pays-Bas, 13, 151.

[2] This JOURNAL, 20, 449.

on the other hand, is an orange, amorphous powder, which decomposes by spontaneous oxidation even *in vacuo*. That these dimolecular substances are compounds and not mixtures is shown by the fact that they were obtained of constant composition from solutions containing the factors in very different proportions. The formation of the dimethylate seems to depend on the conditions of the manufacture. If the product is precipitated with benzol, 2 molecules of the methylate are taken up. If, on the other hand, enough methyl alcohol is present to dissolve the substance so that the salt crystallizes out, there is a tendency to form the monomethylate body even in the presence of a large excess of sodic methylate. The same rule seems to apply to all cases as yet studied—precipitation gives products with more than 1 molecule of the alkaline constituent; crystallization gives those which contain but a single molecule.

The addition-product with sodic phenylate adds another alkaline material to those which give compounds of this class, for, although colored solutions had been obtained with this reagent, the product had not been analyzed heretofore. Hantzsch and Kissel[1] obtained from trinitrobenzol and potassic cyanide a compound containing only 1 molecule of potassic cyanide, $C_6H_3(NO_2)_3KCN$, and also prepared the corresponding acid. In our case 2 molecules were added, as already stated, $C_6H_3(NO_2)_3OCH_3(KCN)_2$. This was not unexpected, as the methyl alcohol solution was precipitated with benzol. The phenylate was precipitated with ether, which seems to produce the same effect as benzol.

In order to see whether a sulphonic group would promote the formation of these compounds in the same way that a carboxyl or third nitro group does, the symmetrical dinitrobenzolsulphonic acid was prepared, as described in a following paper, and from it we obtained the addition-product

$$[C_6H_3(NO_2)_2NaOCH_3SO_3]_2Ba.$$

In looking up colored addition-compounds of this class in the literature, the difficulties already alluded to were encountered, so that we do not feel certain that our list is complete.

[1] Ber. d. chem. Ges., **32**, 3144.

In addition to those described by Drost,[1] of which we spoke at the beginning of this paper, Hantzsch and Kissel[2] have obtained a compound from paranitrobenzylnitramine,

$$C_6H_4NO_2CH_2N_2O_2Na.NaOC_2H_5,$$

and one formed by the action of baric hydrate on trinitrobenzoic acid in aqueous solution, which recalls the addition-compound of baric hydrate and trinitroanisol prepared by Boos and one of us.[3] Hillyer[4] also has obtained a carmine solution by the action of sodic methylate on dinitrophenoxozone, but he did not prepare the solid. The addition-compounds from amines and nitrobenzol derivatives probably belong to the same class as the salts of the quinolnitro acids, but the discussion of them does not fall within the scope of this paper.

Experimental Part.

Constitution of the Colored Substances. (*Quinolnitro Acids.*)

As has been explained in the introduction, the constitution of the colored addition-compounds was determined by the study of the product obtained from trinitroanisol and sodic isoamylate.

Preparation of Trinitroanisol.—The common process for making trinitroanisol from picryl chloride leaves much to be desired. Therefore, after some experiments, we have adopted the following method, which gives a good yield of trinitroanisol with but little expenditure of time and labor, thus converting it into an easily accessible substance. Anisic acid was made from oil of anise by the method of Ladenburg and Fitz,[5] and 5 grams of this substance were added in small portions at a time to a mixture of 40 cc. of fuming nitric acid with the same volume of fuming sulphuric acid of sp. gr. 1.86. After all the anisic acid had been added, the mixture was warmed to 70° for two hours in a flask closed with a glass

[1] Ann. Chem. (Liebig), **307**, 49. In his paper (*Ibid.*, **313**, 299), Drost also describes several color reactions from the corresponding toluol compounds, but gives no analyses of the salts.

[2] Ber. d. chem. Ges., **32**, 3137.

[3] This Journal, **20**, 444.

[4] *Ibid.*, **26**, 361.

[5] Ann. Chem. (Liebig), **141**, 248 (1867).

bulb, care being taken that the temperature did not rise above 70°, as in that case a large amount of picric acid was formed. At the end of two hours the liquid was allowed to cool, then poured into ice-water, and purified by one crystallization from alcohol. The yield of crude anisic acid from the oil of anise is about 75 per cent of the theory, and from this anisic acid about 60 per cent of the theoretical yield of trinitroanisol is obtained.

Addition-Compound of Trinitroanisol and Sodic Isoamylate. (*Sodium Salt of Dinitromethoxyisoamyloxyquinolnitro Acid.*)—To a solution of 2 grams of trinitroanisol in anhydrous benzol a solution of sodic isoamylate was added, prepared by the action of isoamyl alcohol in excess on 0.09 gram of sodium. The amount of trinitroanisol, therefore, was more than twice that needed, if it were mixed with the sodic isoamylate in the proportion of equal molecules. This large excess seemed to be necessary to prevent the formation of addition-compounds containing more than 1 molecule of the isoamylate. For the same reason the mixture was frequently stirred, while it stood for half an hour at ordinary temperatures, to complete the reaction. The bright-red, amorphous precipitate thus obtained was filtered out, washed thoroughly with dry benzol, and after being dried, at first on a porous plate and afterward *in vacuo*, it was analyzed with the following results :

I. 0.3262 gram substance gave 0.0683 gram Na_2SO_4.
II. 0.5073 gram substance gave 0.1116 gram Na_2SO_4.
III. 0.5320 gram substance gave 0.1140 gram Na_2SO_4.
IV. 0.2060 gram substance gave, on combustion, 0.3056 gram CO_2 and 0.0908 gram H_2O. In order to decompose the salt, the substance was mixed with a large excess of a mixture of 8 parts of fused plumbic chromate with one of potassic dichromate, and to lessen the chances of explosion this was spread out in four long porcelain boats.

	Calculated for $C_6H_2(NO_2)_3OCH_3(NaOC_5H_{11})$.	Found. I.	II.	III.	IV.
Na	6.52	6.79	7.13	6.95	....
C	40.80	....	....	....	40.46
H	4.53	....	....	....	4.90

The substance is a bright crimson powder, usually amorphous, but in one experiment it was obtained in short, microscopic prisms. It is decidedly stable for one of these bodies, as it can be kept *in vacuo* for an indefinite time without apparent decomposition, and, even when exposed to the air, it does not deliquesce or change its appearance to a marked extent inside of eight hours. It dissolves in ice-water with a deep-red color, and the solution, if kept at 0°, remains clear for about fifteen minutes. At the end of this time a turbidity begins to appear, and this decomposition continues to take place slowly afterward. Dilute acids decompose it instantly.

As the analyses given above were made with samples from different preparations, there could be no doubt that the substance had a constant composition, but it was possible that it was not a single compound, since it might be a mixture in molecular proportions of $C_6H_2(NO_2)_3OCH_3.NaOCH_3$ and $C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$, which, on analysis, would give such results as we obtained. As our proof of the constitution of this body depended on its individuality, it was necessary for us to remove the doubt suggested above, and we did this by comparing the solubility of our substance with those of its two components, if it were a mixture. Fortunately, the solutions of these bodies in ice-water were stable for a sufficiently long time to admit of determinations near enough for our purpose. The solubilities were tried by the method of Victor Meyer. The substance was stirred with water at 0° for ten minutes, then filtered, and the amount of matter dissolved determined by evaporating with sulphuric acid and weighing the sodic sulphate formed.

Solubility of $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$:

I. 28.69 grams solution, at 0°, yielded 0.0870 gram Na_2SO_4.

II. 50.16 grams solution yielded 0.1113 gram Na_2SO_4.

100 parts of the solution, at 0°, contain the following number of parts:

	I.	II.
$C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$	1.508	1.110

Solubility of $C_6H_2(NO_2)_3OCH_3.NaOCH_3$:

III. 45.08 grams solution, at 0°, yielded 0.0512 gram Na_2SO_4.

IV. 33.92 grams solution yielded 0.0520 gram Na_2SO_4.

100 parts of the solution, at 0°, contain the following number of parts:

	III.	IV.
$C_6H_2(NO_2)_3OCH_3.NaOCH_3$	0.4751	0.6412

Solubility of $C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$:

V. 34.20 grams solution, at 0°, yielded 0.0057 gram Na_2SO_4.

VI. 30.02 grams solution yielded 0.0048 gram Na_2SO_4.

100 parts of the solution, at 0°, contain the following number of parts:

	V.	VI.
$C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$	0.0960	0.0921

These results show wide variations, obviously due to varying amounts of decomposition in the solutions, although the length of time and mode of treatment were kept as nearly uniform as possible in all the determinations. In spite of these experimental errors, however, the results prove that our substance was not a mixture of these two compounds, since the sum of the two highest determinations of the solubility of the components (IV., 0.6412; V., 0.0960) was 0.7372, the lowest solubility for our substance was (II.) 1.1100, which is 0.3728 higher than the solubility corresponding to a mixture, whereas the worst experimental error (between III. and IV.) is 0.1661, less than half of this. A confirmatory argument will be found in the introduction.

The Products of the Decomposition of the Addition-Product from Trinitroanisol and Sodic Isoamylate, $C_6H_2(NO_2)_3OCH_3.NaOC_5H_{11}$.—After a preliminary experiment had shown us that one of the products of decomposition gave off a strong odor of isoamyl alcohol, when boiled with potassic hydrate, we proceeded as follows: Ten grams of the addition-compound were suspended in benzol and shaken with dilute hydrochloric acid (1 : 10). The color disappeared and the solid matter went into solution. The layer of benzol was then washed with water and the benzol evaporated off on the steam-bath. The residue solidified, on standing, to a gummy mass which was washed with about 2 cc. of cold alcohol to remove

the liquid (principally amyl alcohol) that had not dissolved in the water. The amount of alcohol used was kept as small as possible, so as to reduce to a minimum any solution of the solid products, and the quantity of substance removed by this washing was only 0.13 gram from 3 grams of the decomposition-products. The product was then treated with hot ligroin, as we had found that while isoamyl picrate is freely soluble in this solvent, trinitroanisol is comparatively insoluble in it. After the ligroin had dissolved nearly half of the product it was evaporated to dryness, and the crystals thus obtained again extracted with hot ligroin, rejecting the insoluble portion as before. The extract was then recrystallized from hot ligroin until it showed a constant melting-point, which proved to be 68° to 69°, the melting-point of isoamyl picrate. For greater certainty it was dried *in vacuo* and analyzed with the following result :

0.1980 gram substance gave, on combustion, 0.3246 gram CO_2 and 0.0880 gram H_2O.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}$.	Found.
C	44.14	44.70
H	4.34	4.94

This proves that isoamyl picrate is one of the products of the decomposition with acids of the addition-compound of trinitroanisol and sodic isoamylate. That another product is trinitroanisol was made probable by the fact that the crude decomposition-product melted from 62° to 69° (trinitroanisol melts at 64°, the isoamyl picrate at 68° to 69°) and was proved by a determination of the presence of the methoxyl radical in this crude product, which, as it was made quantitatively, also threw light on the relative amounts of the two principal decomposition-products.

I. 0.4091 gram decomposition-products washed with a little alcohol and dried on a porous plate and *in vacuo* gave, by the method of Zeisel,[1] 0.1787 gram argentic iodide.

II. 0.3973 gram substance gave 0.1762 gram argentic iodide.

[1] Monatsh. Chem., **6**, 989; **7**, 406; or Sitzber. Akad. Wiss. Wien., **92**, [2], 1431; **94**, [2], 341.

	I.	II.
Trinitroanisol	45.25	45.94

If the mixture was composed of equal molecules of trinitroanisol and isoamyl picrate, the percentage of trinitroanisol would be 44.83. It would seem probable, therefore, that the two products were formed in equal amounts. In order to get an approximate determination of the quantity of isoamyl picrate formed, 6.7 grams of the decomposition-product, prepared as above, were boiled for two hours with 60 cc. of a solution of potassic hydrate (1 : 10) in a flask with a return-condenser. After the liquid had cooled it was extracted four times with chloroform, the chloroform solution washed thoroughly with water, and dried over fused potassic disulphate. The chloroform was then distilled off carefully and the residue heated until the traces of water, which had escaped the drying agent, had also passed over, keeping the temperature well below the boiling-point of isoamyl alcohol. The residue weighed 0.947 gram, and, after weighing, its boiling-point was found to be 131°, showing that it was isoamyl alcohol. The percentage of isoamyl picrate calculated from this weight of isoamyl alcohol is 48 instead of 55.17 required, if the mixture is composed of equal molecules of the two substances. The agreement is as close as can be expected when the unavoidable losses in the method used are considered.

To meet the objection that the isoamyl picrate in the decomposition-product might have been formed by the action of isoamyl alcohol on the trinitroanisol, after the decomposition with acid had taken place, 0.5 gram of trinitroanisol was heated with a little isoamyl alcohol on the steam-bath for half an hour. After the mixture had cooled, the isoamyl alcohol was removed by washing with a little alcohol and the residue dried on a porous plate and *in vacuo*.

0.2263 gram substance gave, by the method of Zeisel, 0.2126 gram of argentic iodide.

	Per cent.
Trinitroanisol	97.07

This result shows that the action of isoamyl alcohol on trinitroanisol was insignificant in amount, if it acted at all. It is

probable that there is no action whatever, since the difference of 2.93 per cent between the trinitroanisol recovered and that taken is not larger than would be expected from adhering isoamyl alcohol, which could not be wholly removed by the single washing with a little cold alcohol. Thorough washing or crystallization was inadmissible as it might have removed the product of the reaction.

After we had shown that the addition-compound from trinitroanisol and sodic isoamylate gave, on acidification, equal molecules of trinitroanisol and isoamyl picrate, it became of interest to study the effect of the presence of an alcohol, since it seemed probable that this might have an influence on the proportions formed. An experiment was tried, accordingly, in which a considerable amount of methyl alcohol was added to the benzol solution before acidification. The determination of the methoxyl in the product is the one numbered II., already given, and gave essentially the same amount as I., in which no methyl alcohol was used. It seems, therefore, that the presence of the methyl alcohol has no effect on the relative amounts of the products of the decomposition of this mixed addition-compound.

Conversion of the Addition-Compound of Trinitroanisol and Sodic Methylate into the Isoamyl Compound.—The work of Gazzolo and one of us[1] has shown that benzyl picrate is formed by the acidification of the product of the action of benzyl alcohol on the addition-compound of trinitroanisol and sodic methylate, and that trinitroanisol is formed by acidification after methyl alcohol has acted on the dibenzyl addition-compound, but in neither case was the intermediate addition-compound formed by the action of the alcohol analyzed. Boos and one of us[2] analyzed the ethyl-ethylate compound,

$$C_6H_2(NO_2)_3OC_2H_5NaOC_2H_5,$$

formed by the action of ethyl alcohol on

$$C_6H_2(NO_2)_3OCH_3.NaOCH_3,$$

but the percentages of sodium in these compounds are so near

[1] This JOURNAL, **23**, 394.
[2] *Ibid.*, **20**, 449.

each other that the analysis was not of much value, the proof that it was the ethyl compound being furnished in this case (as in the work of Gazzolo) by the isolation of the ethyl picrate. It seemed desirable, therefore, to try the conversion of one addition-compound into another by means of an alcohol, testing the composition of the addition-product formed by analysis. We chose for this work the methyl compound treated with isoamyl alcohol, as the difference between the radicals was sufficiently great to give unmistakable results on analysis. One gram of $C_6H_2(NO_2)_3OCH_3.NaOCH_3$ was mixed with 10 cc. of isoamyl alcohol and the mixture warmed to 70° for about ten minutes, when it was found that the solid had disappeared, giving a deep-red solution. After the liquid had cooled it was poured into a large excess of benzol and the red precipitate washed first with benzol, and afterward many times with cold water. It was then dried at 100° and analyzed with the following result:

0.5070 gram substance gave 0.0948 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OC_5H_{11}.NaOC_5H_{11}$.	Found.
Na	5.62	6.06

$C_6H_2(NO_2)_3OCH_3.NaOCH_3$ would give 7.69 per cent of sodium. There can be no doubt from this result that the isoamylate addition-compound is formed under these conditions.

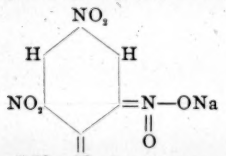
Other Experiments on the Constitution of the Addition-Compounds. (*Quinolnitro Acids.*)—In this section we give some account of our attempts to determine the structure of these colored bodies, before we took up the method already described, which led to the desired result. As these experiments were not fully successful, we describe them only briefly.

The action of aniline on $C_6H_2(NO_2)_3OCH_3.NaOCH_3$ was tried in the hope that it would replace the two methoxyl groups with the formation of an anil,

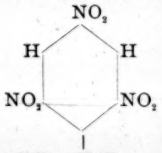
$$C_6H_2(NO_2)_2(NO_2Na)=NC_6H_5.$$

Upon carrying out the decomposition in a flask, and distilling over the methyl alcohol set free into a Zeisel apparatus, it was found that both the methoxyl groups were driven out (found

19.23 and 19.05 per cent of methoxyl instead of 20.87 per cent calculated for $2CH_3O$). The other product of the reaction was a red salt which we did not succeed in purifying[1] even when all the work was carried on in an atmosphere of hydrogen. Upon acidification picrylanilid, $C_6H_2(NO_2)_3NHC_6H_5$, was obtained, which was recognized by its melting-point, 175°, so that the red sodium salt was evidently the picrylanilid salt, $C_6H_2(NO_2)_3NNaC_6H_5$. We also found that there was the strongest similarity between our specimen and one made directly from the anilid. This result can be explained on the quinoid theory by supposing that the first product of the reaction (I.) changed spontaneously into the anilid salt (II.), an



I.



II.

explanation, which seems very probable, whereas, if Hantzsch and Kissel's nitroester acid theory is adopted, it is hard to see why the methoxyl attached to the nitro group should be driven out by aniline, especially since picramide forms an addition-compound with sodic methylate, and it is therefore probable that the corresponding picrylanilid compound would be stable enough to exist. It is obvious, however, that no proof of the structure of the addition-compound can be based on such indefinite results.

Hydroxylamine in alcoholic solution gave a result exactly similar to that just described in the case of aniline, the sodium salt of picrylhydroxylamine, and 2 molecules of methyl alcohol being formed. Phenylhydrazine acted on the substance with too great violence to give good results. At 100° the mixture took fire in a few minutes, and even in the cold the action was so energetic that black, tarry products were formed.

[1] The amount of sodium in two different samples differed by 1 per cent, and both were much higher than that calculated from the formula.

In the hope that replacement of the sodium by an organic radical would form a more stable product, which might give conclusive results with aniline or hydroxylamine, some time was spent in trying the action on

$$C_6H_2(NO_2)_3OCH_3.NaOCH_3$$

of dimethyl sulphate,[1] methyl iodide, acetyl chloride, or benzoyl chloride, but in no case was any result obtained. These experiments confirm the negative results previously obtained by Gazzolo and one of us,[2] and convince us that further experiments in this line are not worth while. Hantzsch and Kissel[3] obtained their acetyl derivative from the free acid.

Experiments were also tried with oxidizing agents on some of the addition-compounds of trinitrobenzol in the hope of removing an atom of hydrogen and the sodium, and thus arriving at a substituted trinitrobenzol. Potassic permanganate gave some not unpromising results, but the work was not continued, because we had proved the constitution of the substances in another way.

Nearly related to these was the attempt to convert Hantzsch and Kissel's addition-product from trinitrobenzol and potassic cyanide,[4] $C_6H_3(NO_2)_3KCN$, into picryl cyanide by the action of bromine. The products of the reaction were black tars, from which we could not isolate any definite substance. A few experiments on the preparation of the as yet undescribed picryl cyanide showed that it is not an easy substance to make.

Experiments along the line which finally led to successful results, consisted in trying to isolate an addition-product of picryl chloride and sodic methylate, which, if it exists, is too unstable for study; and work upon the mixed addition-compound from trinitroanisol and acetoacetic ester. If picryl-acetoacetic ester could be detected in the products of the decomposition of this body, when an acid is added to it, it would be a strong argument for the quinoid formula. Unfor-

[1] Claesson and Lundvall: Ber. d. chem. Ges., 13, 1699.
[2] This JOURNAL, 23, 395.
[3] Ber. d. chem. Ges., 32, 3141 (1899).
[4] *Ibid.*, 32, 3144 (1899).

tunately, we could obtain by the acidification of this substance only unmanageable tars, from which nothing definite could be isolated. By using phenyl picrate or parabromorthonitrophenyl picrate in place of trinitroanisol, the picrylacetoacetic ester,[1] melting at 97° to 98°, was obtained, and the formation of this ester seemed to be preceded by that of colored compounds, but, as these compounds were too unstable to be collected, purified, and dried for analysis, so as to show that they contained both the phenyl and acetoacetic ester radicals, these experiments were of little value for our purpose.

Addition-Compound from Trinitrobenzol and Sodic Methylate. (Sodium Salt of Nitrodimethoxydiquinolnitro Acid.)—Gazzolo and one of us[2] obtained, by the action of sodic methylate (or ethylate) on trinitrobenzol and precipitation of the salt thus formed with benzol, red substances of slight stability, which gave percentages of sodium corresponding to the formula

$$C_6H_3(NO_2)_3(NaOCH_3)_3CH_3OH$$

(or the ethyl compound). As stated in that paper, more analytical data were necessary before any formula could be considered established for these substances, and, accordingly, we took up the study of this subject. When we tried to make the methyl derivative as before with 3 molecules of sodic methylate to one of trinitrobenzol, we got different results from different preparations, varying from 13.10 to 15.02 per cent of sodium, and it was not until we had increased the proportion of sodic methylate to 4 molecules that we got a result of 17 per cent of sodium, corresponding to the 16.94 per cent required by the formula given above. If, on the other hand, the amount of sodic methylate was reduced to 1 molecule, the sodium determinations in the salt came out between the percentages required for the addition of 1 and 2 molecules of sodic methylate. It was evident from these preliminary experiments that the substance was not fit for analysis, either because no constant product was formed or because it suffered decomposition during the preparation for analysis.

[1] Dittrich: Ber. d. chem. Ges., **23**, 2720 (1890).
[2] This JOURNAL, **23**, 391.

Determinations, by the method of Zeisel, of the number of methoxyl groups contained in the substance, gave results showing that there was only one methoxyl group in it instead of the four required by the formula provisionally assigned to it. Further, as this amount was too small to correspond to the percentage of sodium found, we were led to the conclusion that the substance had undergone decomposition between its preparation and analysis. We accordingly prepared two fresh samples, and dried the precipitates formed by the benzol at 60° in a stream of dry hydrogen for half an hour, all the other operations being also carried on as quickly as possible. The analyses gave the following results :

I. 0.3223 gram substance gave 0.1455 gram Na_2SO_4.

II. 0.3100 gram substance gave 0.1426 gram Na_2SO_4.

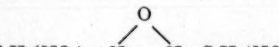
	Calculated for $C_6H_3(NO_2)_3(CH_3ONa)_2$.	Found. I.	II.
Na	14.33	14.62	14.90

There can be no doubt that the substance is formed from the trinitrobenzol by the addition of 2 molecules of sodic methylate.

It is a red, amorphous substance, which decomposes in a few hours, even *in vacuo*. Exposed to the air it deliquesces and becomes tarry in a very short time. If it is heated suddenly to 100° it explodes with great violence, but if the temperature is raised gradually it can be heated to 150° with no apparent change except a slight darkening of the color. Even at this temperature no alcohol is given off.

Decomposition of the Addition-Compound from Trinitrobenzol and Two Molecules of Sodic Methylate.—As stated in the preceding section, this addition-compound decomposes rapidly, even when kept in a vacuum desiccator. In taking up the study of this decomposition we first established the facts that the compound, when acidified immediately after preparation, gave unaltered trinitrobenzol, but after standing three days *in vacuo* no trinitrobenzol was obtained on acidification. Instead of this an amorphous, clay-colored mass was formed, weighing about half as much as the expected trinitrobenzol, while the filtrate had a deep-red color, smelt strongly of formalde-

hyde, and reduced Fehling's solution, or ammoniacal argentic nitrate. In order to obtain a better separation of the products, a second sample, prepared in the same way, was treated with water, filtered, and the filtrate acidified with dilute hydrochloric acid. The residue insoluble in water was recrystallized from strong nitric acid until it showed a constant melting-point, and as this lay at 183° it was evidently the tetranitroazoxybenzol,



discovered by Lobry de Bruyn.[1] The aqueous filtrate gave a strong test for a nitrite. The precipitate formed by the hydrochloric acid was a sticky substance, the nature of which we have not succeeded in determining, but we think it probably contained picric acid, or some similar nitrophenol, as it gave a deep-brown color with an aqueous solution of potassic cyanide, and formed red salts with solutions of the alkalies. The filtrate from this hydrochloric acid precipitate contained apparently a variety of substances, but they were so unmanageable that we did not succeed in recognizing any of them but formaldehyde, which was detected by the properties already mentioned. That the formaldehyde was a principal product of the reaction was shown by a quantitative determination according to Orchard.[2] This gave about quarter the amount which would have been formed if all the methoxyl groups had been oxidized to it. It should be remembered, in this connection, that the specimen had stood *in vacuo* for three days.

An experiment was also tried to determine whether the decomposition, when carried on in air, was attended with a gain or loss in weight, and it was found that the weight of a sample became constant after standing for two months in a desiccator over calcic chloride, and that there had been a loss in weight amounting to 12.66 per cent.

From these observations it seems evident that two or more

[1] Rec. trav. chim. Pays-Bas, **13**, 151.
[2] Chem. Centrbl., 1897, I, 441 ; Analyst, **22**, 4.

reactions take place during the decomposition of the addition-compound of trinitrobenzol and 2 molecules of sodic methylate. One of these consists essentially in the oxidation of one or more of the methoxyl groups to formaldehyde by the oxygen of two nitro groups which form the tetranitroazoxybenzol, and, as this reaction takes place independently of the surrounding atmosphere, it accounts for the slight stability of the substance. A second reaction was indicated by the formation of nitrite and probably of some nitrophenol.

Addition-Compound from Trinitroanisol with Two Molecules of Sodic Methylate, $C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2$.—To a solution of trinitroanisol in anhydrous benzol was added a methyl alcohol solution of sodic methylate in large excess, 3 to 4 molecules of sodic methylate to each molecule of the trinitroanisol. The precipitate appeared in yellow, gummy masses, which were thoroughly washed with benzol, when they became hard and granular. They were dried on a porous plate and then *in vacuo* at 60° for half an hour, and were analyzed immediately with the following result:

I. 0.3672 gram substance gave 0.1526 gram Na_2SO_4.
II. 0.3392 gram substance gave 0.1310 gram Na_2SO_4.
III. 0.3218 gram substance gave 0.1262 gram Na_2SO_4.

	Calculated for $C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2$.	Found. I.	II.	III.
Na	13.13	13.48	12.52	12.72

As the three analyses were made with three different preparations, there can be no doubt that the substance is a definite compound.

Properties of the Sodium Salt of Nitrotrimethoxydiquinolnitro Acid, $C_6H_2(NO_2)_3OCH_3(NaOCH_3)_2$.—It is an amorphous, orange-colored powder, and is much less stable than the corresponding compound containing 1 molecule of methylate, for, although it changes little in appearance on standing *in vacuo*, analyses show that it has undergone a decomposition similar to that just described in the case of the trinitrobenzoldimethylate compound. It is freely soluble in water. It shows no change in appearance, even when heated as high as 150°, but from what has just been said of its behavior *in vacuo*, it is

evident that this observation does not prove that it remains unaltered at this temperature.

Addition-Compound of Trinitroanisol and Potassic Cyanide (Potassium Salt of Nitrodicyandiquinolnitro Acid), $C_6H_3(NO_2)_3OCH_3(KCN)_2$.—A solution of 1.2 grams of trinitroanisol in 20 cc. of methyl alcohol was mixed with 0.5 gram of finely powdered potassic cyanide (that is, somewhat less than 2 molecules of cyanide to each molecule of trinitroanisol), and the mixture shaken for five minutes. It was filtered quickly with the pump and the filtrate diluted with 100 cc. of anhydrous benzol. After standing for a few minutes the precipitate thus obtained was filtered out, washed with benzol, and dried on a porous plate and *in vacuo*, after which it was analyzed with the following result:

I. 0.2491 gram substance gave 0.1176 gram K_2SO_4.
II. 0.2284 gram substance gave 0.1058 gram K_2SO_4.

	Calculated for $C_6H_3(NO_2)_3OCH_3(KCN)_2$.	Found. I.	II.
K	20.95	21.19	20.82

The analyses were made with different preparations.

The addition-compound is a dark, reddish-brown, amorphous substance, freely soluble in water or alcohol, and decidedly unstable.

Addition-Compound of Trinitrobenzol and Sodic Phenylate (Sodium Salt of Nitrodiphenoxydiquinoinitro Acid), $C_6H_3(NO_2)_3(NaOC_6H_5)_2$.—To a solution of 0.5 gram of trinitrobenzol in a mixture of absolute ether and phenol was added the sodic phenylate obtained by treating 0.22 gram of sodium with phenol mixed with a little ether, that is, about twice the theoretical amount of sodic phenylate was used. The mixture was allowed to stand about fifteen minutes with frequent stirring, after which the precipitate was filtered out and washed, at first with absolute ether containing a little phenol, since we found this would dissolve sodic phenylate, and finally with pure ether. The substance was dried on a porous plate and *in vacuo*, and analyzed as soon as possible, with the following results:

I. 0,2086 gram substance gave 0.0653 gram Na_2SO_4.
II. 0.2231 gram substance gave 0.0665 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)_2(NaOC_6H_4)_2$.	Found. I.	II.
Na	10.34	10.15	9.67

The analyses were made with different preparations.

The substance is a bright, brick-red, amorphous powder, and is decomposed immediately by the addition of water. It is, in fact, one of the least stable of these compounds which have been analyzed.

Addition-Compound of Baric Dinitrobenzolsulphonate and Sodic Methylate (*Barium Sodium Salt of Nitrosulphomethoxyquinolnitro Acid*), $[C_6H_3(NO_2)_2NaOCH_3SO_3]_2Ba$.—The sodic methylate, prepared by adding 0.1 gram of sodium to some methyl alcohol mixed with a large excess of anhydrous benzol, was mixed with a solution in methyl alcohol of 0.5 gram of the baric dinitrobenzolsulphonate, $SO_3I(NO_2)_23.5$, prepared as described in a subsequent paper. This gives 4 molecules of the methylate to each molecule of the salt. The solution turned deep-red, but nothing separated even after standing a short time; an excess of benzol was therefore added, which precipitated a dark-red, amorphous mass. This precipitate was filtered out, washed thoroughly with benzol, and then dried on a porous plate and *in vacuo* at 60°. The analysis gave the following results:

I. 0.2072 gram substance gave 0.1070 gram of the mixture of baric and sodic sulphates.

II. 0.2302 gram substance gave 0.1178 gram of the mixture of baric and sodic sulphates.

	Calculated for $[C_6H_3(NO_2)_2NaOCH_3SO_3]_2Ba$.	Found. I.	II.
Ba + Na	24.77	25.21	24.98

The substance is an amorphous, pale salmon-colored powder when dry, but takes on a deep-red color when moistened with benzol, chloroform, or ligroin. This change of color is very striking. It is soluble in water or in methyl or ethyl alcohol, but insoluble in all the other common solvents. It is apparently one of the more stable compounds of this class, as

it undergoes no change in appearance, even when exposed to the air for a long time.

Some attempts to obtain a colored addition-compound from Willgerodt's[1] picrylsulphonic acid led to no definite results, for, although a colored substance was obtained on adding sodic methylate to the free acid, we did not feel certain that this was a derivative of the picrylsulphonic acid, since this substance is decomposed with great ease by alkaline solutions. This color, therefore, might be due to a trinitroanisol derivative, and under these circumstances we did not feel that the subject was of enough importance to spend time in making analyses.

Sodic acetoacetic ester gave a deep-red coloration with phenyl picrate, but we made no attempt to isolate the substance (which may not belong to this class), contenting ourselves with the study of its decomposition-product, which will be described in a later paper.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXXVIII.—THE DECOMPOSITION OF DIAZONIUM SALTS WITH PHENOLS.

By James F. Norris, B. G. Macintire, and W. M. Corse.

Some time ago Hirsch[2] undertook a careful study of the preparation of phenol from aniline by means of the diazo reaction, on account of the fact that the yield of phenol was much less than that required theoretically by the equation usually written to express the decomposition of a diazonium salt with water. It was found that a number of reactions take place simultaneously. Among the products of the decomposition was *p*-oxydiphenyl. This compound was shown to be the product of the action of the diazonium salt on a part of the phenol produced in the decomposition. As a result of the study of this reaction, Hirsch showed that when a cold aqueous solution of a diazonium salt was treated with a large

[1] J. prakt. Chem., [2], **32**, 117 (1885).

[2] Ber. d. chem. Ges., **23**, 3705; **25**, 1973.

quantity of phenol, the diazo compound was extracted from the water. The phenol solution was stable in the cold, but decomposed when heated, with the evolution of nitrogen and the formation of oxydiphenyl, phenyl ether, and ill-defined products which were not isolated. Hirsch endeavored, without success, to extract diazonium salts from an aqueous solution by substances other than phenol. This method of preparing diphenyl derivatives was, therefore, limited to the decomposition of various diazo compounds with this one substance. The method was not a very satisfactory one in that large quantities of phenol were used in the extractions, and a number of fractional distillations were involved.

In studying the preparation of phenol from aniline, in this laboratory, we were led to the view that when a diazonium salt decomposes in the presence of water and a phenol, it reacts to a much larger extent with the phenol than with the water. It seemed possible, therefore, that the preparation of diphenyl derivatives by this reaction might be carried out in aqueous solution, and that the method might be developed into a general one for the preparation of hydroxyl derivatives of diphenyl by using, instead of phenol, other compounds of the same class. To test this view, experiments were carried out with benzenediazonium salts and phenol, pyrocatechin, resorcin, and hydroquinone. It was found that the phenols entered into the reaction when the decomposition of the diazonium compound took place at 75° to 100°, and that good yields of diphenyl derivatives were obtained.

In carrying out the reaction, the phenol, mixed with a small quantity of water and heated to about 90°, was treated cautiously with a cold aqueous solution of the diazonium salt. A vigorous reaction took place, nitrogen was evolved, and a dark, heavy oil separated. When phenol was used, the reaction-product was found to consist of *p*-oxydiphenyl, *o*-oxydiphenyl, phenyl ether, and a tarry mass which could not be purified in any way. The amount of oxydiphenyl obtained was equal to about one-half the weight of aniline used. The reaction furnishes, therefore, a good method for the preparation of this compound. The diphenyl compounds were sepa-

rated from the reaction-mixture by distillation with superheated steam. This method appears to be much more expeditious than fractional distillation, which has been used in the past.

The experiments show that by means of benzenediazonium salts a phenyl group can be introduced readily into a benzene ring which contains an hydroxyl group. As usual, the hydroxyl group sends the entering radical to the para position. In the case of phenol, over 95 per cent of the oxydiphenyl obtained was the para compound. About 5 per cent of an isomer was obtained which, in all probability, was the ortho compound. The substance was not obtained in quantity sufficient to warrant a determination of its structure. In the reaction the hydrogen atom of the hydroxyl group is, to some extent, replaced by phenyl, and an ether results.

The decomposition of benzenediazonium chloride with pyrocatechin proceeded in the same general way. The chief reaction-product was a dioxydiphenyl. The substance formed in the next largest amount was shown to be *o*-oxyphenyl ether, which was formed by the replacement of a hydrogen atom of one of the hydroxyl groups by phenyl. A very small quantity of a substance, which was evidently an isomer of the dioxydiphenyl obtained, was also isolated.

In resorcin there is one position in the benzene ring which is para to one hydroxyl group and ortho to the other. As the orienting influence of both groups is thus, at the same time, directed to this place, it seemed that in this case the reaction would be a smooth one and that isomeric compounds would not be formed. The results of the experiments were surprising, therefore, when it was found that no diphenyl derivatives could be isolated. The only product which was found was the azo compound, notwithstanding the fact that the reaction was carried out at 100°.

Preliminary experiments only have been carried out with hydroquinone. These indicate that the reaction proceeds in a manner analogous to that with pyrocatechin. The chief product of the reaction in this case appears to be *p*-oxyphenyl ether and not a diphenyl derivative, however. This differ-

ence is due, no doubt, to the fact that there is no vacant position para to an hydroxyl group, and, as a consequence, the hydroxyl hydrogen is replaced to a larger extent than is the case with pyrocatechin. To some extent, however, a phenyl group is introduced into the ring and a dioxydiphenyl is formed.

The introduction of a phenyl group into the ring in pyrocatechin and hydroquinone modifies the properties of these compounds. The resulting substances show the reactions of the simpler benzene derivatives, but their reactivity is greatly increased. For example, the phenyl derivative of hydroquinone is oxidized by atmospheric oxygen to a dark-blue compound, which can be reduced by sulphur dioxide to a colorless substance.

The ethers produced in the reaction are stable, and do not reduce an ammoniacal solution of silver nitrate.

The number of hydroxyl groups in the compounds was determined by preparing the acetyl derivatives. In some cases the methyl ethers were also made.

The descriptions of the compounds prepared from hydroquinone will be given in a subsequent paper.

Experimental.

Decomposition of Benzenediazonium Sulphate with Phenol.

The decomposition of benzenediazonium sulphate with phenol was carried out under a variety of conditions. The method finally adopted was as follows: The diazo compound was prepared by treating a cold solution of aniline sulphate, made by dissolving 40 grams of aniline in a mixture of 80 grams of sulphuric acid and 40 cc. of water, with a solution of 36 grams of sodium nitrite in 80 cc. of water. The cold solution was then poured in small portions, with constant shaking, into a large flask containing 80 grams of phenol, which was heated on a boiling water-bath. During the reaction a heavy black oil separated, and much nitrogen was evolved. In order to separate the products of the reaction, the mixture was distilled with steam and the distillate was collected in fractions. In the first experiment ordinary steam

was used and 14 fractions of 100 cc. each were collected. The first nine fractions were found to contain the excess of phenol: In fractions 10 to 14 there were a few needle-shaped crystals which melted at 67°.5 and proved to be *o*-oxydiphenyl. As the major part of the reaction-product was only slightly volatile with ordinary steam, the product of a second decomposition was distilled with superheated steam. The oil formed in the reaction was separated and put into a 500 cc. flask, which was heated to 150° in an oil-bath. The steam, after passing through a $\frac{3}{8}$-inch iron pipe heated in a 30-inch combustion furnace, was at a temperature of 140° to 160°, when it entered the flask. Under these conditions all the oxydiphenyl had distilled over when 700 cc. of water had been collected. The distillate was collected in fractions of 50 cc. each. Numbers 1 to 5 contained an oil, 6 and 7 a semi-pasty mass, and 8 to 14 a white solid. The oil contained the excess of phenol and some *o*-oxydiphenyl, fractions 6 and 7 consisted of a mixture of the ortho and para compounds, and the white solid was almost pure *p*-oxydiphenyl.

The phenol recovered from the first fractions of the distillate weighed 44 grams. Thirty-six grams had, therefore, entered into reaction with the diazo compound, whereas the theoretical quantity required by the following equation for the aniline used is 40 grams:

$$C_6H_5.N_2SO_4H + C_6H_5OH = C_6H_4.C_6H_4OH + H_2SO_4 + N_2.$$

The separation of the isomeric oxydiphenyls was best effected by crystallization from hot petroleum ether (b. p. 50° to 80°) in which the para compound is only slightly soluble in the cold, and in which the ortho compound is much more soluble both hot and cold. *p*-Oxydiphenyl crystallizes well from hot 20 per cent alcohol.

As a result of the decomposition, there was obtained from 40 grams of aniline, 20 grams of pure *p*-oxydiphenyl and 1.5 grams of the isomer. There was a large amount of the reaction-product which was not volatile with steam. It consisted of a black, brittle mass, which dissolved in sodium hydroxide and was precipitated from this solution by the addition of hy-

drochloric acid. The mixture probably contained substances which were formed by the introduction of more than one phenyl group into the benzene ring.

Hirsch noted that an isomer of *p*-oxydiphenyl is formed in the decomposition of benzenediazonium salts with phenol, and assigned to it the ortho structure. No analyses are reported and the properties of the compound are not given. The amount of material obtained by us was not sufficient to warrant an investigation of the structure of the compound. It is, in all probability, an ortho substitution-product produced as a result of the well-known orienting influence of the hydroxyl group. An analysis of the compound melting at 67°.5 resulted as follows:

0.1308 gram substance gave 0.4047 gram CO_2 and 0.0700 gram H_2O.

	Calculated for $C_{12}H_{10}O$.	Found.
C	84.71	84.31
H	5.88	5.91

The compound crystallizes in colorless needles, which are stouter than those of the para compound.

Decomposition of Benzenediazonium Chloride with Pyrocatechin.

As the result of a preliminary experiment it was found that the chief products of the reaction between benzenediazonium salts and pyrocatechin were dioxydiphenyl, *o*-oxydiphenyl ether, and an oil which could not be distilled without decomposition. Of a number of methods of separating the mixture into its constituents which were studied, the one described below was found to be the best.

The diazo compound was prepared by treating a solution of 40 grams of aniline in 100 grams of concentrated hydrochloric acid diluted with 100 cc. of water, with 32 grams of sodium nitrite dissolved in 80 cc. of water. This solution was poured very slowly into a mixture of 50 grams of pyrocatechin and 50 cc. of water, which was heated to about 75°. The product was distilled with steam and the distillate collected in fractions. The first fractions, which contained an oil, were extracted with ether, from which 6.5 grams of phenol were ob-

tained. The solid volatile with steam was found to be *o*-oxydiphenyl ether. About 4 liters of water were necessary to carry over the phenol and the 4.6 grams of ether formed in the reaction. The solution in the flask was decanted from the non-volatile oil and evaporated to a small bulk. The dioxydiphenyl which separated was filtered off, and from the filtrate 21 grams of pyrocatechin were recovered. Thirty-nine grams had, therefore, entered into reaction instead of 47 grams—the theoretical quantity for a reaction between an equal number of molecules of the diazo compound and the phenol.

The non-volatile oil was extracted three times with boiling water. In all, 2.5 liters were required to dissolve the dioxydiphenyl. On cooling, 5 grams of the compound crystallized out and 4 grams in addition were obtained on evaporation. The oil insoluble in water weighed 10 grams. It dissolved in alkali, however, and was, no doubt, a mixture of complex phenols formed by the introduction of more than one phenyl group into the pyrocatechin molecule. An attempt was made to distil this oil. After about 1 gram of a colorless substance had distilled over at 220° to 250°, total decomposition took place. The distillate, after crystallization from a mixture of toluene and petroleum ether, melted at 147°.5 to 148°.5. The substance reduced silver nitrate, gave a white precipitate with lead acetate, and produced a light-green color with ferric chloride, which changed to a reddish-brown on standing and to a deep-violet on the addition of sodium carbonate. The compound was evidently a pyrocatechin derivative, and probably an isomer of the dioxydiphenyl formed as the chief product of the reaction.

The reaction between benzenediazonium salts and pyrocatechin was brought about in a number of ways, in order to determine the effect of the conditions on the yield of the various products of the reaction. The decomposition was effected by raising gradually the temperature of a mixture of the diazo compound and the phenol, by bringing about the reaction at different temperatures, and at 75° and at 100° in the presence of copper powder. In no case were the yields as good as in the experiment described above.

o-Oxydiphenyl Ether.—About 4.6 grams of this substance were obtained from 40 grams of aniline. The compound crystallizes from dilute alcohol in flat needles, and from petroleum ether in well-formed, six-sided needles terminated by domes. It is slightly soluble in hot water, from which it separates, on cooling, in long needles. A cold saturated solution contains 0.11 gram to the liter. *o*-Oxydiphenyl ether melts at 105° to 106° and has an aromatic odor. It is very soluble in carbon bisulphide, benzene, and glacial acetic acid, less soluble in toluene, and only slightly soluble in petroleum ether. It gives no color with ferric chloride, and shows none of the characteristic reactions of pyrocatechin. The results of an analysis follow:

0.1105 gram substance gave 0.3125 gram CO_2 and 0.0553 gram H_2O.

	Calculated for $C_{12}H_{10}O_2$.	Found.
C	77.42	77.08
H	5.37	5.56

A molecular-weight determination, using alcohol as the solvent, gave 176 as the result instead of 186, the theoretical number.

The acetyl derivative was made by heating the phenol with an excess of acetyl chloride. After the product so obtained had been treated with sodium hydroxide it distilled without decomposition at 358° to 360° (uncorr.). The compound is a thick oil, which dissolves in the usual organic solvents. An analysis gave the following results:

0.1251 gram substance gave 0.3386 gram CO_2 and 0.0607 gram H_2O.

	Calculated for $C_{14}H_{12}O_2$.	Found.
C	73.68	73.82
H	5.26	5.39

The methyl ether of *o*-oxydiphenyl ether was prepared by heating a solution of the phenol in methyl alcohol with the calculated quantities of potassium hydroxide and methyl iodide. The compound crystallizes from methyl alcohol in long, flat, six-sided crystals. It dissolves in the ordinary sol-

vents and melts at 77°. The formation of this compound and of the monoacetyl derivative described above, shows that the structure assigned to the *o*-oxydiphenyl ether is correct. An analysis of the methyl ether gave the following results:

0.1074 gram substance gave 0.3063 gram CO_2 and 0.0589 gram H_2O.

	Calculated for $C_{13}H_{12}O_2$.	Found.
C	78.00	77.78
H	6.00	6.09

Dioxydiphenyl.—Nine grams of this compound were obtained from 40 grams of aniline. The crude substance which was separated from the original reaction-product by extraction with water was dark-brown in color and somewhat gummy. In this condition it is best purified by crystallization from hot petroleum ether, in which it is only slightly soluble. It melts at 136° to 136°.5 and boils above 360° without decomposition. It is very soluble in alcohol, chloroform, and ether, less soluble in carbon bisulphide, petroleum ether, and hot water. A cold, saturated, aqueous solution contains 1.6 grams per liter. The compound gave a light-green color with ferric chloride, which changed to a reddish-brown on standing, and which was changed to a deep-violet on the addition of sodium carbonate. It reduces silver nitrate, and gives a precipitate with lead nitrate and with bromine water. No marked coloration is produced when the substance is heated with phthalic anhydride and sulphuric acid. An analysis gave the following results:

0.2048 gram substance gave 0.5826 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_{12}H_{10}O_2$.	Found.
C	77.42	77.53
H	5.37	5.54

The diacetyl derivative was obtained by heating the phenol with an excess of acetyl chloride. It crystallizes from alcohol in long, six-sided crystals, which melt at 77° to 77°.5. The analytical results were as follows:

0.1285 gram substance gave 0.3341 gram CO_2 and 0.0628 gram H_2O.

	Calculated for $C_{16}H_{14}O_4$.	Found.
C	71.11	70.91
H	5.18	5.43

Two dioxydiphenyls are possible as the result of the introduction of a phenyl group into the benzene ring of pyrocatechin. In one compound the group introduced is ortho and meta to the two hydroxyl groups; in the other it is para and meta to these groups. An attempt was made to determine which of these structures belonged to the dioxydiphenyl formed as the chief product of the decomposition of the diazonium salt with pyrocatechin. The phenol was converted into the corresponding dimethyl ether, which was then oxidized. It was expected that in this way the phenyl group would be converted into carboxyl and, as a result, a dimethoxybenzoic acid obtained. If the phenyl group occupied the position para to one of the hydroxyl groups, the oxidation-product would be veratric acid, a well-described compound. The oxidation was brought about under a variety of conditions with chromic acid and with potassium permanganate. Only when the last-named substance was used could any oxidation-product be isolated, which in this case proved to be benzoic acid. The structure of the compound was not established, therefore, but on account of the usual directing influence of the hydroxyl group and the results with phenol, it is highly probable that the substance is 3,4-dioxydiphenyl.

BOSTON, MASS., Nov. 1, 1902.

XXXIX.—THE ACTION OF ZINC ON TRIPHENYLCHLORMETHANE.

BY JAMES F. NORRIS AND LLORA R. CULVER.

In an investigation of some new applications of the Friedel and Crafts reaction, which was carried out in this laboratory nearly four years ago, the condensation of carbon tetrachloride with benzene was studied under conditions different from those which had been used in the past. It was thought that

the change in conditions might lead to the formation of tetraphenylmethane, instead of triphenylmethane, the compound which had been obtained as the product of this reaction. The substance formed, however, proved to be triphenylchlormethane.[1] As the compound could be obtained readily in this way in a high state of purity, and as it proved to be a very reactive substance of unusual interest, we undertook a thorough study of it and its reactions. Among the experiments undertaken was an attempt to condense the compound with brombenzene by means of sodium, and thus prepare tetraphenylmethane. We obtained, as the result of the reaction, not the expected product but a compound containing oxygen. This substance and the cause of its formation were under investigation when papers appeared by Gomberg[2] on the preparation of triphenylchlormethane, and the action of metals on this compound. As our work was well in hand at this time, a preliminary paper was published from this laboratory outlining what had been done and what was under investigation at that time. This was thought to be advisable, as our results in part supplemented those of Gomberg. We had isolated an intermediate compound in the preparation of triphenylchlormethane from carbon tetrachloride, which had not been obtained by Gomberg. This substance, which has the formula $Al_2Cl_6.2(C_6H_5)_3CCl$, appeared of interest as it was the first compound of aluminium chloride with an alkyl chloride to be isolated. It has proved of interest since its discovery. It was also shown in the same paper that, under certain conditions, triphenylchlormethane reacts with sodium, contrary to the observations of Gomberg.[3] This paper was replied to by Gomberg,[4] who claimed priority and disputed our right to continue our line of work.

The brilliant discovery by Gomberg of the highly unsaturated compound formed by the action of zinc on triphenylchlormethane, led to conclusions as to the structure of the substance which were at variance with the accepted views of

[1] This JOURNAL, **28**, 54.
[2] J. Am. Chem. Soc., **22**, 752, 757.
[3] *Ibid.*, **22**, 758.
[4] *Ibid.*, **23**, 109.

the valence of carbon. As the unsaturated compound was of such unusual interest, we continued our investigation to discover if any explanation of the remarkable reaction, other than that of trivalent carbon, could be found. We did this as the point did not appear to us to be proved, and as our own experiments had put us in a position where we could go on with the work started before Gomberg's first paper appeared.

In a second paper by one of us,[1] the view was put forward tentatively that the unsaturated compound had the structure $(C_6H_5)_2C{=}C_6H_4$, it being formed by the elimination of hydrogen chloride from triphenylchlormethane. As evidence for this view, the statement was made that when zinc reacted with triphenylchlormethane dissolved in ethyl acetate, hydrogen was evolved. It was shown that zinc had no action on ethyl acetate and, consequently, the hydrogen must come from the triphenylchlormethane.

In a reply to this paper it was pointed out by Gomberg[2] that, when ethyl acetate which had been dried over phosphorus pentoxide was used in the reaction, no hydrogen was evolved, but that when the solvent was dried in the usual way over calcium chloride, the gas was formed. The observed evolution of hydrogen was due, as a consequence, to the action of the water present on the triphenylchlormethane, by which hydrochloric acid was liberated. This acid, in turn, reacted with the zinc to form hydrogen. This work of Gomberg showed that the experimental evidence put forward by one of us was faulty, in that care had not been taken to use an absolutely dry solvent.

The study of the action of metals on triphenylchlormethane was continued, nevertheless, as the work which had already been done had brought to light a number of facts overlooked by Gomberg, which needed explanation. With the view of testing every hypothesis that suggested itself before accepting the explanation of trivalent carbon, an attempt was made to determine quantitatively the substances which entered into the reaction and the products formed.

[1] This JOURNAL, **25**, 117.
[2] *Ibid.*, **25**, 317.

At the beginning of the work it was found that the statement of Gomberg[1] was incorrect, that when the reaction between zinc and triphenylchlormethane took place in benzene solution, the metal reacted quantitatively according to the following equation :

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C- + ZnCl_2.$$

During the course of the reaction a thick, dark mass separates, which Gomberg assumed to be a compound of benzene and zinc chloride. In determining the amount of chlorine removed by the metal, this mass was shaken with water and the halogen determined. The amount found was equal to that in the triphenylchlormethane used. From this the conclusion was drawn that all the chlorine was in the form of zinc chloride. In our earliest experiments we found that zinc chloride, like aluminium chloride, forms a compound with triphenylchlormethane, and that the dark, gummy mass formed in the reaction consisted in part of this compound, for when it was decomposed with water, triphenylcarbinol was set free. The single quantitative experiment on which Gomberg based his theory in his first paper was, therefore, manifestly incorrect, and there were no data as to the amounts of zinc and triphenylchlormethane which entered into reaction. Gomberg, in a later paper, briefly mentioned this mistake, but he has reported no further work to test this point.

When a solution of triphenylchlormethane in ethyl acetate is treated with zinc, care being taken to exclude oxygen, a highly unsaturated compound is formed, which readily absorbs oxygen and is thus converted into an insoluble peroxide of the formula $(C_6H_5)_3C—O—O—C(C_6H_5)_3$. The amount of this compound formed, according to Gomberg, varies usually between 75 and 80 per cent of the theoretical amount calculated from the triphenylchlormethane used. The filtrate from the peroxide, which contains about one-fourth of the organic reaction-product, has not received in the past the attention that it deserves. As triphenylmethane, triphenylcarbinol, and an oil are at times present, an investigation of the cause of the formation of these substances must be made before the reac-

[1] J. Am. Chem. Soc., **22**, 761.

tion, which is evidently a very complex one, can be exactly interpreted.

The substances mentioned above were found in the filtrate when precautions were taken to avoid the presence of moisture during the reaction between the zinc and the organic halide. Triphenylchlormethane was converted in part into triphenylmethane. It was important to discover, if possible, whence came the hydrogen that had replaced the chlorine. It is possible that a reaction might take place according to the following equation:

$$2(C_6H_5)_3CCl + Zn = (C_6H_5)_2C{=}C_6H_4 + (C_6H_5)_3CH + ZnCl_2.$$

Such a reaction would be analogous to that between zinc and another tertiary halide:

$$(CH_3)_3CI + Zn = (CH_3)_2C{=}CH_2 + (CH_3)_3CH + ZnI_2.$$

Some time ago Nef[1] studied the action of zinc on triphenylbrommethane. In all the experiments reported, triphenylmethane was the chief product of the reaction. An amorphous substance was also formed. Nef explained the reaction by assuming that the metal caused the elimination of hydrobromic acid from triphenylbrommethane, and that an unstable compound of the formula

$$(C_6H_5)_2C{-}C_6H_4$$

was produced. This substance was reduced in part to triphenylmethane and in part converted by polymerization into a red tar. When 5 grams of the bromide dissolved in 20 cc. of absolute ether were treated with 2 grams of granulated zinc at 65°, 1.6 grams of triphenylmethane were obtained.

As a determination of the amount of triphenylmethane formed in our experiments showed that but small quantities were present, it was evident that the main reaction was not that written above. It is highly probable that the reaction described by Nef does take place to some extent, even at room temperature, and that, in this way, the triphenylmethane and the oil noted above were produced.

[1] Ann. Chem. (Liebig), 309, 169.

Nef's experiments were carried out at temperatures varying from 65° to 150° where polymerization of the compound

$$(C_6H_5)_2C{=}C_6H_4$$

probably took place. As it seemed that such a compound might be capable of existence at room temperature, and might prove to be the triphenylmethyl of Gomberg, an attempt was made to remove hydrogen chloride from triphenylchlormethane without the use of heat. To this end the halogen compound was treated with pyridine, as it is claimed that this compound readily removes hydrogen chloride from acetyl and benzoyl chlorides.

Five grams of triphenylchlormethane and 1.42 grams of pyridine were dissolved in a small quantity of ethyl acetate and set aside. At the end of a few days large, pink crystals, which melted at 167° to 167°.5, had separated. These were washed with ether, dried at 105°, and analyzed. The percentages of chlorine in two different samples were 10.05 and 9.72, respectively. The theoretical for a compound of the formula $(C_6H_5)_3CCl.C_5H_5N$ is 9.93 per cent. The compound does not lose weight over sulphuric acid, and is decomposed by water with the formation of triphenylcarbinol and pyridine.

The experiment did not lead to the desired result. Nef had previously removed hydrogen bromide from triphenylbrommethane by means of triethylamine, but the reaction was carried out in boiling benzene and a tar was produced.

While the work of Nef furnishes an explanation of the manner in which triphenylmethane is produced in the reaction, no experimental work so far reported has furnished any explanation of the formation of triphenylcarbinol. As this substance is formed in appreciable quantities, the reaction between zinc and triphenylchlormethane cannot be correctly interpreted until the presence of the carbinol is explained. A study of the quantities of zinc and triphenylchlormethane which entered into the reaction, and the amount of oxygen absorbed by the unsaturated compound produced, furnished a reasonable explanation of this point.

In making a quantitative study of the reaction a special piece of apparatus was used. A 30 cc. Erlenmeyer flask was fitted with a rubber stopper through which passed two tubes bent at two right angles. These tubes were connected by means of heavy rubber tubing to two Hempel gas burettes containing mercury. By raising and lowering the side tubes, the gas confined could be passed from one burette, through the flask, into the other burette. In order to prevent any leak at the joints, there were fitted to the burettes and the neck of the flask, by means of rubber stoppers, pieces of glass tubing of large diameter. These tubes were placed in such positions that they formed cups around the rubber connectors. The cups were then filled with mercury which completely covered the joints. During an experiment the enclosed gas was kept under a slightly reduced pressure, as an inward leak of gas was impossible. A layer of concentrated sulphuric acid, which floated on the surface of the mercury in one of the burettes, served to dry the gas admitted.

In performing an experiment, the burettes were partially filled with oxygen and a weighed quantity of carefully purified triphenylchlormethane was placed in the small flask. A measured quantity of ethyl acetate, which was free from acid, water, and alcohol, was next added. A small glass tube containing a weighed quantity of pure granulated zinc was then introduced into the flask. The tube was flat on the bottom so that it stood in the liquid and thus prevented the contact of the metal with the ethyl acetate. The flask was next connected with the burettes by means of the stopper, and the outside glass jacket put into place and filled with mercury. When all was tight, the gas enclosed in the apparatus was passed through the flask from one burette to the other. In this way it was dried by coming in contact with the sulphuric acid and became saturated with ethyl acetate vapor. Readings of the temperature and volume were made until a constant state of affairs had been reached. The flask was now carefully shaken, the tube containing the zinc was overturned, and the metal thus brought into contact with the solution. Reaction set in immediately, and the solution assumed a dark-

yellow color. In a short time the peroxide began to separate. The rate of absorption of the oxygen was noted by frequent readings of the volume of the gas. At first the gas was absorbed quite rapidly, but toward the end of the experiment the absorption was very slow. The yellow color of the solution slowly decreased until it had almost entirely disappeared, when the reaction was complete. When the absorption ceased, the flask was removed and the zinc left was determined. It was not found difficult to separate the metal from the precipitated peroxide. The small amount of this substance which adhered to the zinc was removed by dissolving it in hot carbon tetrachloride. The difference in the weight of the zinc before and after the reaction was evidently the amount which had entered into the reaction. The weight of the peroxide formed in the reaction was also determined. The precipitate was filtered from the reaction-mixture and washed with a little ethyl acetate, in which it is not appreciably soluble. The part removed from the zinc by carbon tetrachloride was recovered and added to the main amount. As zinc oxide was found to be a product of the reaction, and as it was collected with the peroxide, the latter was weighed, then treated with hydrochloric acid, and weighed again. These data gave the amounts of peroxide and zinc oxide formed.

The original filtrate from the peroxide, which contained the products of the reaction soluble in ethyl acetate, was diluted with ether, shaken with water to remove zinc chloride, and evaporated to dryness. In all cases triphenylcarbinol and a small quantity of an oil were formed. In some cases triphenylmethane was also found. When this was the case the filtrate was much richer in oil, which had a pleasant aromatic odor. The mixture left on evaporation was dissolved in benzene from which the carbinol and the triphenylmethane crystallized. When the solution had gone to dryness the crystals were removed and pressed on an absorbent plate in order to free them from the oil. The crystals were then washed with a little cold benzene. To separate the hydrocarbon from the carbinol the mixture was treated with concentrated sulphuric acid in which the carbinol is soluble. The carbinol is pre-

cipitated by diluting the acid solution with water. The part insoluble in the acid was crystallized from benzene, and was identified as triphenylmethane by the melting-point of the crystals formed, and the change in their melting-point when crystallized from alcohol. The carbinol was readily obtained in pure condition by crystallizing it from carbon tetrachloride. The oily product of the reaction was obtained in very small quantities, and as it was evidently a mixture it was not investigated.

A series of experiments was also made in which the oxygen absorbed was not determined. In this case the flask in which the reaction was carried out was closed by a cork carrying a drying-tube. The results of a number of experiments are tabulated below. In the columns marked "theoretical zinc" and "per cent zinc used" are given the amount required by Gomberg's equation:

$$2(C_6H_5)_3CCl + Zn = 2(C_6H_5)_3C- + ZnCl_2.$$

No.	$(C_6H_5)_3CCl$ used.	Zn used.	Theoretical zinc.	Per cent Zn used.	Per cent peroxide obtained.	Oxygen in peroxide.	Oxygen used.	Weight of product in filtrate.
1	2.721	0.369	0.318	116	52	0.081	0.116	1.044
2	1.091	0.252	0.127	198	29	0.018	0.061	0.637
3	1.940	0.329	0.226	145	48	0.053	0.100	0.875
4	2.121	0.417	0.248	169	38	0.046	0.098	1.183
5	1.470	0.218	0.172	127	70	....	....	0.407
6	2.084	0.353	0.243	145	53	....	....	0.863
7	1.091	0.165	0.127	130	37	....	....	0.624
8	1.013	0.225	0.118	190	35	....	....	0.649
9	1.090	0.171	0.127	135	49	....	....	0.525

An examination of the results shows that the reaction between zinc and triphenylchlormethane is a very complicated one and that very slight changes in the conditions of the experiment have a marked influence on the result. The most evident facts are, first, that much more zinc is used than is called for by Gomberg's equation; second, that much more oxygen is absorbed than is contained in the peroxide; and

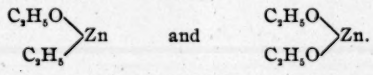
third, that the percentage of peroxide obtained is less than that found by Gomberg. These quantitative results must be interpreted before the nature of the reaction between zinc and triphenylchlormethane can be understood.

An explanation of the large amount of zinc used suggests itself. The usual action of zinc on alkyl halides is of the nature of that represented by the following equations:

$$C_2H_5I + Zn = C_2H_5—Zn—I;$$
$$2C_2H_5—Zn—I = Zn(C_2H_5)_2 + ZnI_2.$$

In this case 1 molecule of the halide reacts with 1 atom of zinc. In Gomberg's equation, 2 molecules react with 1 atom of zinc. If the formation of a zinc alkyl took place completely in the case of triphenylchlormethane, twice the amount of zinc calculated from Gomberg's equation would be used. If it took place in part in this way and in part according to Gomberg's explanation, the amount of metal used would be between 100 and 200 per cent. For some time we have been studying in this laboratory the action of metals on a number of halogen derivatives, and have found that zinc forms compounds with a number of chlorides. It is possible that it may form to some extent a zinc alkyl with triphenylchlormethane. Such a compound would no doubt be a very reactive substance.

Zinc ethyl reacts with oxygen to form the compounds:



The first of these compounds decomposes with water into zinc hydroxide, ethane, and alcohol. The second gives zinc hydroxide and alcohol. If a zinc alkyl is formed with triphenylchlormethane, or if the intermediate compound

$$(C_6H_5)_3C—Zn—Cl$$

is produced, it would probably absorb oxygen and be converted into a substance which, on further decomposition, would yield triphenylcarbinol.

This explanation of the formation of triphenylcarbinol,

which was found in the filtrate in every experiment, also serves to explain the fact that much more oxygen is absorbed than is contained in the peroxide. In experiment No. 2, for example, 0.061 gram of oxygen were used, whereas the peroxide found contained only 0.018 gram. In this experiment the carbinol formed was determined. The amount of oxygen in this compound was 0.0392 gram. The sum of the oxygen in the peroxide and carbinol was, accordingly, 0.0575 gram, which is a little less than the total amount used, 0.0609 gram. This relation held in the other experiments, the sum of the oxygen in the peroxide and the carbinol being nearly equal to the total oxygen used. It seems highly probable, therefore, that the carbinol formed in the reaction is produced as a result of the action of oxygen on some unstable compound in solution.

If a zinc alkyl is formed as suggested here, zinc hydroxide would be one of the products of its decomposition. This compound was shown to be present in some of the experiments. The amounts obtained varied between 0.007 and 0.047 gram.

The fact that the yield of peroxide obtained by us is much less than that obtained by Gomberg is a striking one. According to Gomberg a low yield of peroxide, when ethyl acetate is used as a solvent, is due to the presence of water or alcohol which causes the decomposition of the triphenylchlormethane with the formation of hydrochloric acid. This explanation does not apply to our results, as no hydrogen was evolved as the result of the action of the liberated acid on the zinc. If the gas had been given off, in the apparatus used by us, it could not escape and, consequently, it would have been measured with the enclosed oxygen. The decrease in the volume of gas, which was taken as a measure of the oxygen absorbed, would have been, accordingly, smaller than it should have been. The experimental results are in just the opposite direction, however. As the percentage of peroxide obtained decreased, the ratio of the oxygen absorbed to the peroxide increased. The results also show that as the amount of zinc used increases, the amount of peroxide formed decreases. The high percentage of zinc used was accompanied also by a

high percentage of carbinol. If it is assumed that a zinc alkyl is formed, these facts indicate that an increase in the quantity of the alkyl is accompanied by a decrease in the amount of peroxide and an increase in the amount of carbinol. We must conclude, therefore, that the hypothetical zinc alkyl is not the compound from which the peroxide is produced by the action of oxygen. The carbinol, however, is probably formed in this way.

A quantitative study of the reaction between triphenylchlormethane and zinc, carried as far as could be done conveniently, does not serve to answer definitely the question as to the structure of the highly unsaturated compound discovered by Gomberg. The work done throws a great deal of light on the reaction and proves that it is of a very complex nature. The facts brought forward do not prove or disprove the correctness of the conception of trivalent carbon, but where so many reactions are taking place simultaneously there is a chance that there may be subtle changes going on which the experimental data, so far collected, do not lead us to suspect. It must be said, however, that none of the facts can be used as evidence against the existence of triphenylmethyl. The equation written by Gomberg may express a part of the truth, but evidently another reaction of importance is also involved. It is also probable that the reaction which leads to the formation of the carbinol takes place more readily in ethyl acetate than in benzene solution. This investigation was carried out with ethyl acetate as solvent, as the products of the reaction are soluble in the acetate. When benzene is used, the separation of a compound containing triphenylchlormethane complicates the study of the reaction.

Work is now in progress to test the view already put forward by one of us that a hydrogen atom in a benzene ring is involved in the reaction. The investigation will be continued along this line, as the experimental evidence put forward in support of the view that the unsaturated compound from which the peroxide is formed contains a trivalent carbon atom, does not appear to the writer sufficient to warrant the acceptance of such a radical assumption.

BOSTON, MASS., Dec. 1, 1902.

XL.—THE ACTION OF ZINC ON BENZOYL CHLORIDE.

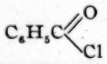
By James F. Norris and D. R. Franklin.

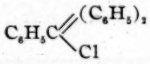
The great importance of correctly interpreting the reaction that takes place between zinc and triphenylchlormethane has led us to study the action of the metal on a number of organic halogen compounds. An examination of the literature brings out the fact that at times zinc causes a simple condensation by removing 2 atoms of the halogen from 2 molecules of the organic compound. In some cases an unstable zinc alkyl is formed. In other cases the zinc compound produced is stable. Very often the metal causes the elimination of halogen hydride and complex condensations result.

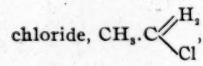
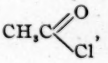
The reactions as studied in the past have been carried out at elevated temperatures when the zinc chloride produced in the reaction has a marked effect. It seemed probable that a review of some of the older work in this field might lead to new facts of importance which would serve to explain the results of work already reported and to throw some light on the important reaction, the study of which has led to such interesting results and conclusions.

Among the reactions studied is that which takes place between zinc and benzoyl chloride. This work was undertaken on account of the analogy between benzoyl chloride and triphenylchlormethane. At first sight the similarity between these compounds may not appear, as one is an acid chloride, whereas the other is an alkyl chloride. This difference is more one of name than of fact. A study of the reactions of triphenylchlormethane shows that the compound resembles an acid chloride, notwithstanding the fact that its structure indicates no analogy. Triphenylchlormethane reacts readily with water and is thus converted into a hydroxyl compound. With alcohol it reacts as an acid chloride, and the chlorine is replaced by an ethoxyl group. The resulting compound, although an ether in structure, is readily decomposed. The analogy between benzoyl chloride and triphenylchlormethane

is indicated by writing the structures of the compounds as follows:





In the triphenylmethane derivative we have two phenyl groups in place of an oxygen atom. Two phenyl groups are not as negative as an oxygen atom and we would expect, therefore, to find some differences between the reactions of the compounds. The reactivity of the chlorine atom in compounds built on the above type is, no doubt, dependent on the nature of the radicals to which the halogen is joined. For example, when we replace two hydrogen atoms in ethyl chloride,  , by a negative oxygen atom,  , we change in a most marked degree the reactivity of the chlorine atom. By the change, we increase the negative character of the molecule to such an extent that the compound becomes unstable and readily exchanges its chlorine for a less negative hydroxyl group. It seems to the writer that the positive or negative character of the group to which a chlorine atom is joined is the main factor which determines the degree of reactivity of the halogen with other compounds. The difference, therefore, between an acid and alkyl chloride is no sharper than that between an acid- and base-forming element.

From this point of view the analogy in reaction between triphenylchlormethane and benzoyl chloride is easy to understand. The difference between the compounds is due to the fact that two phenyl groups are not the exact equivalent of one oxygen atom. If two groups could be found whose combined character equals an oxygen atom, a compound containing these groups and built on the above type would probably act exactly as benzoyl chloride does, and the hydroxyl derivative of such a radical, while having the structure of a tertiary

alcohol, would be a true acid.[1] As it is possible to vary the positive or negative nature of the phenyl group by introducing substituting atoms or groups around the ring, it is highly probable that two groups can be found whose combined action is equal to that of an oxygen atom. Such an investigation is now being carried out in this laboratory. If two such groups can be found, it is probable that we can obtain a substance analogous to carbon monoxide. Such a compound would be a methylene derivative in which there is present a stable bivalent carbon atom. The results of experiments to test the above views will be published later.

Leaving out of account the hypothesis put forward above, it is certain that the reactions of triphenylchlormethane resemble those of benzoyl chloride and, accordingly, interesting results should be obtained as a consequence of the study of the action of zinc on benzoyl chloride. From one point of view the results would be very helpful. If, in this case, the metal removes the chlorine quantitatively, according to the reaction

$$2C_6H_5.COCl + Zn = 2C_6H_5CO + ZnCl_2,$$

a benzoyl group would be produced. We would expect such a group to polymerize and produce dibenzoyl, a well-known compound. Gomberg's equation for the action of zinc on triphenylchlormethane is as follows:

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_3C- + ZnCl_2.$$

The view is put forward that the radical set free exists as such and does not double up on account of stereo-chemical considerations. The three phenyl groups take up so much room around the carbon atom that there is no chance for two such radicals to unite. The fact that no one has succeeded, in spite of much effort, in preparing hexaphenyl-

[1] From the above point of view triphenylcarbinol is a very weak acid. This conception is in accord with the view very recently put forward by Baeyer and Villiger (Ber. d. chem. Ges., **35**, 3015), who have arrived at this conclusion from an entirely different standpoint. Gomberg (Ber. d. chem. Ges., **35**, 2397) considers the carbinol a weak base. Both conceptions are probably correct. The compound resembles to some extent the hydroxides of certain inorganic elements which are in the borderland between the well-defined acid- and base-forming elements. It is probable that by a change in the nature of the radicals the basic property of the compound can be increased to such an extent that a true carbon base will be produced.

ethane is evidence in favor of this view.[1] With benzoyl-chloride, however, this state of affairs cannot exist. Dibenzoyl is known. It was of great interest, accordingly, to see if by the action of zinc on benzoyl chloride dibenzoyl was produced, when the reaction was carried out in the absence of oxygen, and in such a way that no hydrochloric acid was given off. If benzil is produced in this way, Gomberg's view is well taken. If, however, the halogen is removed quantitatively by the metal, and benzil is not produced, the experiment is good evidence that the reaction between zinc and benzoyl chloride is of an entirely different nature from what we might expect, and that the reaction between zinc and triphenylchlormethane may not be as simple as has been supposed.

Zincke studied the action of zinc on benzoyl chloride in 1873.[2] He found that the chloride reacted violently with the metal and large quantities of hydrogen chloride were evolved. Dilution with benzene did not alter the results. Under the latter circumstances the formation of benzophenone was expected. The product of the reaction in both cases proved to be a tarry mass from which were obtained benzoic acid, a little benzophenone, and a brown substance melting at 145° to 146°, the nature of which was not established. The reaction was a violent one and led, no doubt, to deep-seated changes.

As the action of zinc on triphenylchlormethane was investigated in ethyl acetate solution (see preceding article), we studied the action of zinc on benzoyl chloride under the same conditions. Under these circumstances the temperature of the reaction-mixture did not exceed that of the room and no hydrogen chloride was evolved. A much longer time is required for the reaction to complete itself than is required in the case of triphenylchlormethane.

[1] Since the above was written Ullmann and Borsum (Ber. d. chem. Ges., 35, 2877) have reported the preparation of a hydrocarbon by the reduction of triphenylcarbinol by means of zinc and hydrochloric acid in acetic acid solution. The evidence put forward in favor of the fact that the compound is hexaphenylethane appears satisfactory. The method of preparing the hydrocarbon was entirely analogous to that used to prepare tetraphenylethane from diphenylcarbinol. The existence of hexaphenylethane seems to the writer to be a good argument against the possibility of the existence of triphenylmethyl.

[2] Bull. soc. chim., 19, 516; Ber. d. chem. Ges., 6, 137.

Experiment 1.—As the reaction proceeded very slowly in the cold, an experiment was made to determine whether the mixture could be heated without causing any secondary reactions. A mixture of 15 grams of benzoyl chloride and 10 cc. of ethyl acetate was heated under a return condenser with a few grams of zinc chloride. The solution soon assumed a dark-brown color and a gas was given off which burned with a green flame. Evidently ethyl chloride was formed. When the reaction-product was distilled, a small quantity of acetyl chloride was obtained. The thermometer rose slowly to 249° when some benzoic acid distilled over. A charred mass was left after the volatile products had distilled off.

In an attempt to discover in what way zinc chloride brought about such a deep-seated decomposition, it was found that the chloride formed a compound with benzoyl chloride, which was very reactive. When ethereal solutions of the two substances are mixed an oil soon precipitates, which yields zinc chloride and benzoyl chloride when treated with water. This new compound reacts with a number of substances with which benzoyl chloride will not react. The important part played by zinc chloride in a number of reactions is no doubt similar to that played by aluminium chloride. In both cases the "catalytic agent" produces the final results by first forming an intermediate addition-product which is very reactive. The composition and properties of the compound of zinc chloride and benzoyl chloride and similar substances will be investigated.[1]

As a result of the above-described experiments the reaction between zinc and benzoyl chloride was allowed to take place at room temperature. It was shown that below 25° zinc chloride did not cause a reaction to take place between benzoyl chloride and ethyl acetate.

[1] Gomberg (Ber. d. chem. Ges., **35**, 2398) gives as an argument in favor of the basic character of the triphenylmethyl group the fact that its chloride forms double salts with the chlorides of certain metals. After we had shown that triphenylchlormethane formed a compound with aluminium chloride, Gomberg prepared a number of such double salts. It seems to us that the formation of such salts cannot be taken as evidence of basic properties, since such a compound as benzoyl chloride forms double salts with aluminium bromide and the chlorides of aluminium, titanium, and zinc.

Experiment 2.—A mixture of 30 grams of benzoyl chloride and 20 cc. ethyl acetate, free from alcohol, acid, and water, was allowed to stand with granulated zinc for one week. The solution was then shaken with water to remove zinc chloride and dried over anhydrous sodium sulphate. As a preliminary experiment showed that the reaction-product crystallized with difficulty, the product was distilled. After a small quantity of benzoyl chloride and benzoic acid had distilled over, the thermometer rose rapidly to 360°. When the product remaining in the flask was distilled under a pressure of 100 mm. 10 grams of an oil were obtained, which boiled at 258°. The oil soon changed to a mass of crystals which melted at 41° to 43°. On recrystallization from alcohol a melting-point of 42° was obtained. The compound was shown to be benzoic anhydride by treating it with aniline, when benzanilide was obtained. A small residue remained in the distillation-flask. No benzil—the substance expected as the product of the reaction, if the metal has caused a simple doubling up of two benzoyl groups—was obtained. The formation of benzoic anhydride could be easily explained, however. The experiment had been carried out in the presence of air. If the metal had caused the removal of the halogen from the acid chloride with the consequent formation of a benzoyl radical, this group instead of polymerizing to benzil may have absorbed oxygen and thus passed into the anhydride. The reaction would be parallel, in this case, to that which takes place, according to Gomberg, between zinc and triphenylchlormethane, the only difference being that in the case of the benzoyl group one oxygen atom is absorbed and an oxide is formed, whereas with triphenylmethyl 2 atoms produce a peroxide. With triphenylchlormethane, the hydroxyl derivative of the radical, triphenylcarbinol, is one of the products of the reaction. With benzoyl chloride, the hydroxyl derivative of benzoyl, benzoic acid is also produced. The results of this experiment show a striking analogy to those with triphenylchlormethane. To test this explanation of the course of the reaction, a quantitative experiment was next carried out.

Experiment 3.—The reaction was brought about in an apparatus in which the amount of oxygen absorbed could be measured. After standing forty-eight days, about 180 cc. of oxygen had been absorbed and 6.8 grams of zinc had passed into solution. If the reaction takes place according to the following equations,

$$2C_6H_5COCl + Zn = 2C_6H_5CO- + ZnCl_2,$$
$$2C_6H_5CO- + O = (C_6H_5CO)_2O,$$

when 1 atom of zinc enters into the reaction 1 atom of oxygen will be absorbed. The quantitative results show that only about one-seventh of the oxygen required enters into the reaction. The reactions which take place are, therefore, not those written above.

The product formed in this experiment was not distilled, as it was thought that the anhydride obtained might be a secondary product formed in the distillation of the reaction-product. Further, dibenzoyl, although it distils with only slight decomposition, might undergo change under the conditions of our experiments. The product left after the evaporation of the solvent consisted of a few crystals mixed with a brown, oily substance. The crystals proved to be benzoic acid. Extraction of the mass with alcohol yielded more benzoic acid, and caused the brown substance to change to a powder which was almost insoluble in alcohol. No benzoic anhydride and no benzil were obtained. These facts confirmed the view that the anhydride was produced as the result of the destructive distillation of the original reaction-product. The brown powder could not be brought to crystalline condition. It melted at 125° to 130°. When distilled, benzoic acid and anhydride were obtained.

Experiment 4.—The relation between the amounts of zinc and benzoyl chloride which reacted with one another was next determined. Thirty grams of the acid chloride dissolved in 50 cc. of ethyl acetate were treated with an excess of zinc and allowed to stand at room temperature. After a number of days the decrease in the weight of the zinc was determined. The weighings were continued until the loss in

weight between two tests was a very small amount. At the end of thirty-two days the amount of zinc used was 100.6 per cent of the amount required according to the equation

$$2C_6H_5COCl + Zn = 2C_6H_5CO- + ZnCl_2.$$

The solution of the reaction-product was washed with water and dried. One-fifth was allowed to crystallize, with the result which was obtained in the previous experiment. The remaining four-fifths, when distilled, yielded 4 grams of benzoic acid, 7.2 grams of benzoic anhydride, and 4 grams of residue. It is evident that the benzoic anhydride and a part of the benzoic acid were produced as a result of the decomposition of the brown amorphous substance, which was the main product of the reaction.

Experiment 5.—Although only a small quantity of oxygen was absorbed, it seemed possible that this amount might have prevented the polymerization of the benzoyl radical to benzil. Accordingly, the reaction was allowed to proceed in the absence of air. In this case, also, no benzil was obtained when the product of the reaction was subjected to fractional crystallization. The substances obtained were, as before, benzoic acid and the brown amorphous powder, which had no sharp melting-point. In two experiments the reaction-products were distilled. Twenty grams of benzoyl chloride, dissolved in 30 cc. of ethyl acetate, were treated with a large excess of zinc (72 grams), as it was found that the speed of the reaction was determined by the amount of the metal present. At the end of eight days the bottle containing the mixture was opened and connected with a vessel containing oxygen. About 30 cc. of the gas were absorbed. It was found that the zinc used in the reaction was 111 per cent of that required by the equation given above. When the ethyl acetate solution of the reaction-product was shaken with water to remove zinc chloride, a small amount of zinc hydroxide was formed. Upon distillation, 3.5 grams of benzoic acid and 9 grams of benzoic anhydride were obtained. In another experiment, using the same amounts of substances, the zinc which went into solution was 98 per cent of that required if the reaction is between

2 molecules of the acid chloride and 1 atom of the metal. In still another experiment, when the reaction was allowed to go on for forty-eight days, more zinc was used than is required by this ratio.

A number of unsuccessful attempts were made to obtain the chief product of the reaction, the brown amorphous solid, in a state of purity. A study of this substance would, no doubt, throw a great deal of light on the nature of the reaction.

Conclusions.

1. At room temperature zinc removes chlorine from benzoyl chloride without the formation of hydrogen chloride.

2. The molecular quantities of the two substances which react are approximately those represented by the equation

$$2C_6H_5COCl + Zn = 2C_6H_5CO- + ZnCl_2.$$

3. When the reaction is carried out in the presence of oxygen only a small quantity of the gas is absorbed.

4. When the reaction-product, after the removal of zinc chloride, is subjected to crystallization, benzoic acid and an amorphous solid are obtained. When distilled, the products obtained are benzoic acid, benzoic anhydride, and a small undistillable residue.

5. When the reaction is carried out either in the presence of, or in the absence of, oxygen no dibenzoyl is formed.

6. In some of the experiments more zinc was used than is required by the equation given above and zinc hydroxide was formed when a solution of the reaction-product was treated with water. These observations indicate that to some extent an organo-metallic compound was formed. If such a compound was produced it may have reacted with the benzoyl chloride and thus complicated the reaction. It seems probable that a study of the reaction from this point of view might lead to an explanation of the unexpected results obtained.

7. Finally, the conclusion can be drawn that the reaction between zinc and benzoyl chloride is such a complicated one that it cannot be interpreted by the use of the facts so far discovered.

BOSTON, MASS., Nov. 1, 1902.

Contributions from the New York Agricultural Experiment Station.

II.—METHODS FOR THE ESTIMATION OF THE PROTEOLYTIC COMPOUNDS CONTAINED IN CHEESE AND MILK.

By Lucius L. Van Slyke and Edwin B. Hart.

When milk-casein and its salts, or paracasein, in cheese, and its salts are acted upon by dilute acids or alkalies under certain conditions, or by enzymes, or by micro-organisms, the proteid bodies are split up, forming a variety of complex cleavage-products. The extent and intensity of such proteolytic changes are measured by the proportions and kinds of the different compounds resulting from the decomposition. In the ripening process that takes place in cheese, we have an instance of extensive proteolysis in the case of the nitrogen compounds of the fresh cheese, due probably to the combined action of dilute acid, enzyme, and micro-organisms. In our study of the causes that produce cheese ripening and of the conditions that influence the process, we were at the start brought face to face with the difficulty involved in the lack of satisfactory methods for making quantitative separations and determinations of the products of cleavage formed. While we have well-elaborated methods for estimating the amount of casein and albumin in fresh milk, these are of little aid in studying the products of their decomposition. Little attention has been given to the development of methods that are applicable to the products occurring in this field. Serious difficulties are involved in such a study. First, we know at present only in an extremely meagre and vague way the chemical constitution of milk-casein and its allied compounds. As regards the constitution of the various compounds formed by the proteolysis of casein, we are largely in the dark, except in the case of some of the simpler ones. In the second place, this field is difficult to study, because the quantities of individual compounds that we have to work with are usually very small.

Under these conditions methods of quantitative separation must, at best, be regarded as largely empirical and more or

less tentative. Instead of estimating individual compounds, about which our chemical knowledge is complete, we are compelled, in a large degree, to estimate groups of compounds, the individual members of which we know, for the most part, incompletely, or not at all.

From the peptic digestion of casein, Chittenden has separated the proto- and deuterocaseoses,[1] and, from a tryptic digestion, a deuterocaseose and a peptone.[2] Alexander[3] has separated heterocaseose from a peptic digestion of casein, but only in small quantities. Many investigators have observed paranuclein or pseudonuclein, the insoluble residue remaining from the peptic digestion of casein or paracasein. Emil Fischer and P. A. Levene[4] have obtained pyrrolidine-α-carbonic acid from a tryptic digestion of casein.

By hydrolysis of casein with hydrochloric acid, Cohn[5] obtained 1-parahydroxyphenyl-α-amidopropionic acid (tyrosine), 1-α-amidoisobutylacetic acid (leucine), amidosuccinic (aspartic) acid, α-amidoglutaric (glutamic) acid, a pyridine derivative, and ammonia. By the same means, Emil Fischer[6] has recently isolated, among the monoamido acids, in addition to products previously obtained by others, amidovaleric acid, phenyl-α-amidopropionic acid (phenylalanine), pyrrolidine-α-carbonic acid, and probably amidoacetic acid (glycocoll).

Among the crystallizable end-products which have been found in ripening cheese are the following: Tyrosine, leucine, histidine, α,ε-diamidocaproic acid (lysine), tetramethylenediamine (putrescine), pentamethylenediamine (cadaverine), lysatine, guanidine probably, and ammonia. Most of these products have been recently reported by Winterstein and Thöny[7] as being found in Emmenthaler cheese. Excepting cadaverine and guanidine, they had also been previously found, though not reported, in American cheddar

[1] Studies in Physiol. Chem., Yale Univ., **2**, 156 (1884–5).
[2] *Ibid.*, **3**, 66 (1887–8).
[3] Ztschr. physiol. Chem., **23**, 411 (1898).
[4] *Ibid.*, **33**, 170 (1901).
[5] Ber. d. chem. Ges., **29**, 1785 (1896).
[6] Ztschr. physiol. Chem., **33**, 151 (1901).
[7] *Ibid.*, **36**, 28 (1902).

cheese in this laboratory. It is very probable that other amido compounds will be found, sooner or later, among the products formed by the tryptic, if not the peptic, digestion of milk-casein and of cheddar cheese.

In cheese we find, earlier or later during the ripening process, a series of compounds and groups of compounds, which, so far as we know at present, appear in about the following order of succession: (1) Paracasein, (2) unsaturated paracasein lactate, (3) paranuclein (pseudonuclein), (4) caseoses (albumoses), (5) peptones, (6) compounds of amido acids, and (7) ammonia. After the early stages of ripening, we have present at the same time all these different compounds and groups.

We will consider methods for the separation and estimation of the proteolytic products found, first in cheese, and, second, in milk, following the general order indicated above. It may be well to say at the outset that, in dealing with the separation of nitrogenous bodies so complex in composition as those mentioned above and occurring in very variable quantities, we can, at present, only hope to approximate accurate quantitative results in the study of milk and cheese problems. While we have in the Nencki method a very accurate means of estimating ammonia, the methods used in separating peptones from amido compounds cannot be relied upon to give us more than approximate results.

I. METHODS FOR THE SEPARATION AND ESTIMATION OF THE NITROGEN COMPOUNDS OF CHEESE.

1. *Obtaining Sample of Cheese.*

A sample of cheese is obtained for analysis by means of a cheese-trier, which enables one to secure a round plug of cheese about 0.5 inch in diameter and 4 to 6 inches long. Four or five plugs are drawn, one within a short distance of the center of the cheese, one about an inch from the outer circumference, and the others at points equidistant between the two previously taken. Samples thus taken represent practically all different conditions existing in the cheese.

After each plug of cheese is removed, about an inch of the end having the rind is cut off and the rest placed in a well-stoppered, large-mouthed sample-bottle. The end with the rind is dipped once or twice in melted paraffin and then carefully replaced in the cheese, being pushed in a little below the surface. After all the plugs have been taken and the ends properly replaced in the cheese, some of the melted paraffin is poured over the surface to fill up and surround the depressions made by replacing the ends of the plugs. This treatment generally insures the exclusion of molds, and prevents abnormal loss of moisture in the portions of cheese near the holes left by the removal of the cheese plugs. This is a matter of much importance when one intends to keep the same cheese for one or two years for systematic examination.

When one has taken all the plugs of cheese needed, the analysis should not be long delayed. The cheese in the bottle is cut into small pieces with a spatula and stirred within the bottle, in order to mix the whole into as homogeneous a mass as possible.

2. *Determination of Total Nitrogen in Cheese.*

We weigh out 1 or 2 grams of the cheese, prepared as described above, for the determination of total nitrogen, and treat it according to the Kjeldahl-Gunning method, modified as follows: When the solution has become partially digested add a piece of copper sulphate about as large as an ordinary pea. Unless this is done it will take a long time to convert the organic nitrogen completely into ammonia.

3. *Extraction of Water-soluble Products.*

In a porcelain mortar we thoroughly mix 25 grams of our cheese sample, prepared as indicated above, with about an equal bulk of clean quartz sand. This mixture is transferred to a 450 cc. Erlenmeyer flask, to which we add about 100 cc. of distilled water at a temperature of 50° C. The flask is then placed on a water-bath, or in some place where it can be kept at a temperature of 50° to 55° C., and is allowed to stand for half an hour, being vigorously shaken from time to time. The

liquid portion is then decanted through a filter of absorbent cotton into a 500 cc. flask. The residue is again treated with 100 cc. of water, heated, agitated, and the liquid decanted as before. This process is repeated until the filtrate, after being cooled to room temperature, amounts to 500 cc., exclusive of the fat, which usually is present at the top of the liquid.

The cotton filter mentioned is made of two layers of absorbent cotton prepared as follows: In a glass funnel we place some absorbent cotton to the depth of about one inch, moisten this with water, in order to compact it, and then above this place another layer of cotton of the same thickness. Upon this we pour our portions of cheese extract. This kind of filter allows rapid filtration without the aid of a pump, and is as effective in every way as paper, which requires half a day or more for complete filtration of 500 cc. of extract. Several samples of cheese can be extracted at the same time. The upper layer of cotton holds all solid particles and can be returned to the flask for extraction with salt solution.

The method of making a water extract of cheese, as described above, insures the complete removal of all water-soluble nitrogen compounds present in the cheese without danger of coagulating any soluble proteids. The use of water at room temperatures is not, in our experience, equally effective in making a complete extraction of the water-soluble products. Under some conditions, as in the early stages of ripening cheese at low temperatures, small amounts of a body which is precipitated by heat in neutral solution are extracted by water. We are unable to say at present whether this body consists of acid salts of paracasein or of heterocaseose, which are practically insoluble in water, or whether it is some other compound. The temperature of 50° C. also has the advantage of arresting further peptic or tryptic action during the extraction. The use of acids in extracting cheese is to be avoided, since a small amount of acid will not only precipitate the soluble nuclein, but may form salts with paracasein, which are somewhat soluble in a slightly acid solution. The amount of dissolved paracasein salts under such circumstances

depends on the amount of acid used and the time of extraction.

4. *Determination of Total Water-Soluble Nitrogen.*

For the determination of the amount of total water-soluble nitrogen we take 50 cc. of the water extract, prepared as described above, equivalent to 2.5 grams of cheese, and treat it according to the Kjeldahl method for determining nitrogen.

5. *Determination of Nitrogen in the Form of Paranuclein (Pseudonuclein).*

To 100 cc. of the water extract, equivalent to 5 grams of cheese, we add 5 cc. of a 1 per cent solution of hydrochloric acid, and warm the mixture on the water-bath at 50° to 55° C., until complete separation takes place, as shown by a clear supernatant liquid. The precipitate is filtered, washed with water, and is then, with the filter-paper, treated by the Kjeldahl method to determine the amount of nitrogen. The amount found equals the nitrogen present in the form of paranuclein (pseudonuclein).

In our early work we used 2 or 3 cc. of a saturated solution of alum for this determination, for the reason that, in the separation of casein in milk, we had used this reagent successfully, but at the time we did not know the nature of the body we were precipitating from our water-solution of cheese. Later, when we had studied it and learned its character, we found, on comparing precipitations by the use of alum and by hydrochloric acid, that alum gave high results, undoubtedly precipitating some caseoses. In 27 comparative trials with water extracts of different cheeses, we found in the alum precipitate nitrogen varying from 0.2 to 0.337 per cent of the cheese, and averaging 0.269 per cent, while the nitrogen in the hydrochloric acid precipitate varied from 0.046 to 0.145 per cent of the cheese, and averaged 0.085 per cent. The nitrogen precipitated by alum in these 27 cases was from 2.1 to 5.5 times as much as that precipitated by hydrochloric acid, the average of all being 3.2. Since hydrochloric acid is known to precipitate paranuclein completely, we are

justified in assuming that the alum precipitates other compounds, and this is confirmed by other work, showing that when alum is used as the first precipitant, we get smaller quantities of caseoses in the filtrate than we do when we use hydrochloric acid as the precipitant of paranuclein. Alum appears to resemble zinc sulphate as a precipitant of proteids.

Paranuclein (pseudonuclein) results from the breaking down of casein or paracasein, and is always found in the water extracts of ripening cheese, whether salted or unsalted. It may, perhaps, be regarded more accurately as a residue, and probably should not be counted as one of the products to be used in measuring the extent of cheese-ripening. This is undoubtedly the same body as Chittenden's dyspeptone,[1] which he found as an insoluble residue in a pepsin-hydrochloric acid digestion of casein.

6. *Determination of Nitrogen in the Form of Proteids Coagulable by Heat in Neutral Solution.*

The filtrate from the preceding determination, 5, is made neutral with dilute caustic potash, using phenolphthalein as indicator. It is then heated at the temperature of boiling water until any coagulum that forms settles completely, leaving a clear, supernatant liquid. The precipitate is washed with water and its nitrogen determined by the Kjeldahl method. In our experience, such a precipitation rarely occurs except in the case of cheese ripened near freezing-point. The nature of this body we have not yet investigated.

7. *Determination of Nitrogen in the Form of Caseoses (Albumoses).*

The filtrate from the preceding determination, 6, is treated with 1 cc. of 50 per cent sulphuric acid, saturated with pure zinc sulphate, and then warmed to about 70° C., until the caseoses separate completely and settle. The mixture is allowed to cool and is then filtered. If filtered hot, there will occur a further separation of caseoses in the filtrate on cooling. The precipitate is washed with a saturated solution of zinc sulphate made slightly acid with sulphuric acid. The

[1] Studies in Physiol. Chem., Yale Univ., 3, 66 (1887–8).

nitrogen in the precipitate is determined by the Kjeldahl method.

For the determination of caseoses, the use of ammonium sulphate was exclusively employed, until Bömer[1] proposed the use of zinc sulphate, which possesses a distinct advantage in enabling one to determine nitrogen directly in the precipitate or filtrate. This method has been employed in the estimation of caseoses, also by the Wisconsin Agricultural Experiment Station. In the present state of our knowledge of this class of compounds, zinc sulphate must be regarded as the most available reagent for their quantitative separation.

8. *Determination of Nitrogen in the Form of Amido Acid Compounds.*

The amido acid compounds are determined in the filtrate from the precipitation of peptones, 9. For the removal of peptones, three reagents have been commonly used, (1) tannin and sodium chloride, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. After the removal of peptones the filtrate contains amido acid and ammonia compounds. After determining the amount of total nitrogen in this filtrate and then the amount of nitrogen present in the form of ammonia, as obtained in 10, page 167, we subtract the amount of ammonia nitrogen from the combined amount of amido acid and ammonia nitrogen, and thus obtain the amount of amido acid nitrogen. In the following section, 9, we describe the methods involved in removing peptones by the different reagents, and the efficiency of each reagent.

9. *Determination of Nitrogen in the Form of Peptones.*

(1) *By Tannin and Sodium Chloride.*—We place 100 cc. of our water extract of cheese in a 250 cc. graduated flask, add 1 gram of sodium chloride and a solution containing 12 per cent of tannin, until 1 drop added to the clear supernatant liquid gives no further precipitate. We then dilute to the 250 cc. mark, shake, filter through a dry filter, and determine the amount of nitrogen in 50 cc. of the filtrate by the Kjeldahl method. This gives us the amount of nitrogen in the form of amido

[1] Ztschr. anal. Chem., 5, 569 (1895).

acid and ammonia compounds. The amount of nitrogen in the form of peptones is determined by difference, that is, by subtracting from the amount of total nitrogen in the water extract the combined sum of the amounts of nitrogen found in 5, 6, 7, 8, and 10.

The combination of tannin and salt has been settled upon by us as the most satisfactory for the separation of casein-derived peptones from amido acid compounds in milk and cheese analysis, when, as is commonly the case, we have large amounts of amido acid compounds relative to peptones. We have confirmed Schjerning's[1] results, showing that this reagent does not precipitate the monoamido acid compounds, such as leucine, tyrosine, aspartic acid, glutamic acid, and amidovaleric acid, nor does it precipitate histidine, arginine, lysine, cadaverine, putrescine, lysatine, or ammonia. In our work the tannin-salt solution has nearly as great a precipitating power as phosphotungstic acid, precipitating 93.3 per cent of the total nitrogen compounds present in a sample of fresh milk. In a study of ripened cheese, it precipitated the uncrystallizable end-products, caseoses and peptones, so completely that no further trouble was experienced in separating the crystallizable end-products.

It is well to record here the fact that when precipitation of peptones with tannin salt solution is attempted in a mineral acid solution, no precipitation occurs. It is only in neutral solution that more complete precipitation takes place.

The chief objection to the use of tannin-salt solution as a means of separating caseoses and peptones from amido acid compounds and ammonia is that it does not completely precipitate peptones. Hence, when we use the reagent for this separation, we commonly leave some peptones to be estimated as amido acid compounds, the amount of peptones thus being made smaller, and the amount of amido acid compounds larger, than the quantity actually present. Under our discussion of the use of phosphotungstic acid as a reagent for separating these classes of nitrogen compounds, we will give for comparison some results secured by each of the two reagents.

[1] Ztschr. anal. Chem., 39, 545 (1900).

(2) *By Phosphotungstic Acid with Sulphuric Acid.*—In a 250 cc. graduated flask we place 100 cc. of the water extract of cheese, add 100 cc. of water and then 5 cc. of strong sulphuric acid. To this we add phosphotungstic acid of 30 per cent strength, until 1 drop gives no further precipitation in the clear supernatant liquid. We then dilute to the 250 cc. mark and filter through a dry filter. In 50 cc. or 100 cc. of this filtrate we determine the amount of nitrogen by the Kjeldahl method, and then the amount of peptones is obtained by difference.

Phosphotungstic acid has come into very general use in this country and in Europe as a means of separating peptones from amido acid compounds in work with cheese and milk. The work of Stutzer[1] and of Bondzynski[2] agrees in showing that phosphotungstic acid is a complete precipitant of casein, caseoses and peptones, while in their experience it does not precipitate the amido acid compounds or ammonia. Freudenreich and Jensen in all their work, even of recent date, have used this reagent in the cold as a means of separating peptones from amido acid compounds. Babcock, Russell, and Vivian, in this country, have used it, as well as tannin, designating the different precipitates as "peptones by phosphotungstic acid" and "peptones by tannin."

In the introductory portion of this paper, when mentioning different cleavage-products of casein, we included among them the hexone bases, *viz.*, arginine, histidine, and lysine, and, in addition, certain compounds resulting from their cleavage, such as putrescine and cadaverine, and also pyrrolidine-*a*-carbonic acid, all of which are precipitated by phosphotungstic acid. While not all these products have been separated from ripening cheese, it is probable that they will be sooner or later. We shall soon publish results of work done in this laboratory, showing in normal ripening cheese the presence of histidine, lysine, putrescine (derived from arginine),[3] and Siegfried's lysatine, which is also precipitable by phosphotungstic acid. The quantities of these bases that can be de-

[1] Ztschr. anal. Chem., 35, 493 (1896).
[2] Landw. Jahrb. der Schweiz, (1894).
[3] A. Ellinger: Ber. d. chem. Ges., 31, 3183 (1898).

rived from casein are not to be neglected, since, for example, in a hydrochloric-acid cleavage 15.4 per cent of the nitrogen of the products is split off in the hexone bases. Bondzynski has used phosphotungstic acid in hot solution with arginine and finds the precipitate soluble when hot, separating out on cooling, and this statement we can confirm, the solution, however, being complete only on boiling. In the case of lysine, histidine, and putrescine, the phosphotungstic acid precipitate fails to redissolve completely at the temperature of the water-bath or on boiling. This behavior renders worthless the use of phosphotungstic acid as a reagent for the separation of peptones from those amido acid compounds that are precipitated by it.

We have seen that tannin-salt solution fails to precipitate peptones completely and that phosphotungstic acid precipitates, in addition to peptones, some amido acid compounds. When, therefore, we use these two reagents in precipitating solutions that contain both peptones and amido acid compounds, as in the case of normal ripening cheese, we should expect to find the amount of nitrogen compounds left in the filtrate less with phosphotungstic acid than with tannin. This is found invariably to be the case. Vivian[1] has published some results obtained with nine different cheeses, which illustrate this point. We give his figures in the following table.

Table I.—Comparison of Phosphotungstic Acid and Tannin-Salt Solution in Precipitating the Nitrogen Compounds Contained in Water Extracts of Cheese.

No. of sample.	Percentage of nitrogen in cheese found in filtrates after precipitation by Phosphotungstic acid.	Tannin-salt solution.
1	1.08	1.54
2	1.00	1.26
3	0.82	1.12
4	0.63	0.65
5	0.67	1.16
6	1.69	1.87
7	0.95	1.08
8	1.10	1.36
9	1.22	1.42
Average,	1.02	1.27

[1] Ann. Rept. Wis. Expt. Sta., 16, 171 (1899).

In connection with the above results, nothing was stated in regard to the history of the cheeses used in the work. We have been able to study the action of phosphotungstic acid and tannin-salt solution in connection with samples of cheese that were under known well-controlled conditions, enabling us to know something of the general character of the proteolytic changes taking place. We placed 25 grams of cheese curd in each of several Erlenmeyer flasks, added 50 cc. of water, and sterilized the contents by heat. We then added 0.5 gram of concentrated lactic acid, in order to convert the paracasein into unsaturated paracasein lactate.[1] To some of the flasks thus prepared we added sterilized pepsin, and to others sterilized rennet extract. For this purpose the enzymes were prepared as follows: We dissolved 600 milligrams of Parke, Davis & Co.'s aseptic pepsin in 25 cc. of water, added 0.5 per cent of formalin (containing 40 per cent of formaldehyde), and let the solution stand until bacteriological examinations, made by Mr. H. A. Harding, showed the absence of living organisms. The mixture was then diluted to 100 cc. with water, and to each flask containing cheese we added 10 cc. of this sterilized pepsin solution. One thousand parts of the mixture in each flask thus contained one part of pepsin.

In preparing the sterilized solution of rennet, we diluted 5 cc. of Hansen's rennet extract to 25 cc. with water, added 0.5 per cent of formalin, proved the completeness of sterilization by bacteriological examinations, diluted to 100 cc., and added 10 cc. of this preparation to each flask containing cheese.

The flasks thus prepared were kept at 15°.5 C. The analytical results given below were obtained at the end of two and four weeks. In this work we had only the enzymes of pepsin and of rennet pepsin acting upon our proteid. Under these conditions, especially in the given length of time, we should not expect the formation of any considerable amount of amido acid compounds precipitable by phosphotungstic acid. The results obtained are given in the following table:

[1] N. Y. Agr. Expt. Sta., Bull. No. 214, p. 67 (1902).

Table II.—Comparison of Phosphotungstic Acid and Tannin-Salt Solution in Precipitating the Nitrogen Compounds Formed by Peptic Digestion of Cheese.

No. of sample.	Per cent of nitrogen in cheese found in filtrate after precipitation by Phosphotungstic acid.	Tannin-salt solution.
1	0.10	0.45
2	0.10	0.44
3	0.150	0.645
4	0.175	0.685
5	0.10	0.48
6	0.08	0.46
7	0.16	0.73
8	0.16	0.70
Average,	0.128	0.574

In every case except one, the amount of nitrogen not precipitated by tannin-salt solution was more than four times the amount obtained by phosphotungstic acid. No ammonia was present in any case. In view of these widely differing results in relation to the amounts of amido acid compounds found, the questions may be asked, Which reagent more nearly represents the amount of amido compounds actually present? Does the tannin-salt reagent fail to precipitate the peptones completely, thus allowing the unprecipitated peptones to be counted among the amido acid compounds? Or does the amount of nitrogen in the filtrate in case of this reagent really represent amido acid compounds? Does the phosphotungstic acid precipitate some of the amido compounds simultaneously with the peptones, thus cutting out a part of the amido acid compounds, and counting that part among the peptones? Or is there in the cheese only the small amount of end-products indicated by the action of the phosphotungstic acid?

While we did not by individual isolation determine to what extent amido compounds were present, we are justified in believing that such compounds were not yet present in the cheese in any appreciable degree; and, hence, the figures obtained with phosphotungstic acid are much nearer the truth than those obtained by tannin-salt precipitation. We will state

our reasons for this belief. The amido compounds precipitated by phosphotungstic acid are known to be chiefly the diamido compounds, while the monoamido compounds are precipitated little, if at all. Hence, the compounds found in the filtrate of a phosphotungstic acid precipitation are mainly monoamido compounds. Now let us assume temporarily that the amounts of nitrogen in the tannin-salt filtrate, given in the table above, represent the total amido compounds, free from peptones. Then, since the monoamido compounds are represented by the amounts of nitrogen obtained in the phosphotungstic acid filtrate, the difference between the two sets of figures, that is, those obtained by tannin-salt solution and those obtained by phosphotungstic acid, represents the amount of diamido compounds. Taking the average of the results given in the table above, the nitrogen of the total amido compounds is 0.574 per cent of the cheese, while the nitrogen of the monoamido compounds is 0.128 per cent of the cheese, thus leaving the difference as the nitrogen of the diamido compounds, equivalent to 0.446 per cent of the cheese. According to these figures, the monoamido compounds constitute about 22 per cent of the entire amount of amido bodies, while the remainder, 78 per cent, represents largely diamido compounds. In this case the ratio of monoamido to diamido compounds is as 1 to 3.5. Keeping these data in mind, we will call attention to some work done by Hart[1] in studying the end-products of cleavage formed by the action of hydrochloric acid on casein. He found that the diamido compounds formed less than 20 per cent of the total amido compounds, so that the ratio of monoamido to diamido compounds was as 1 to 0.25 or less. In other words, the monoamido compounds were greatly in excess of the diamido compounds, or just the reverse of what we find to be the case in the results embodied in the table above, based on the assumption that the nitrogen in the tannin-salt filtrate represents the total amido compounds and nothing more. The most obvious and rational explanation of this discrepancy, observed in the ratio of monoamido to diamido compounds, is that it is wrong to assume

[1] Ztschr. physiol. Chem., **33**, 347 (1901).

that the tannin-salt filtrate contains only amido compounds and not any peptones. Withdrawing that assumption, then, and allowing that the nitrogen in the tannin-salt filtrate represents some peptones as well as the amido compounds, how can we tell in this particular case the true amount of amido compounds in the cheese? Unquestionably, the results with phosphotungstic acid more nearly represent the truth in regard to the amido compounds, because, under the conditions of the experiment, we should expect very small amounts of amido compounds, if any; and, in this particular case, the amounts are so small as practically to indicate the absence of amido bodies altogether. From this it may be seen that it is possible for the tannin-salt reagent to give results that are decidedly misleading.

(3) *By Bromine with Hydrochloric Acid.*—To the filtrate from the zinc sulphate precipitate in 7, we add 2 or 3 drops of strong hydrochloric acid, and then bromine until the liquid becomes saturated and there remains, after vigorous agitation, an undissolved globule of bromine amounting to 0.5 to 1 cc. This is allowed to stand over night. The precipitate is then filtered and washed with saturated bromine water. The nitrogen in the precipitate is then determined by the Kjeldahl method, and is called nitrogen in the form of peptones, the filtrate containing the amido acid compounds and ammonia.

The use of chlorine by Rideal and Stewart[1] in precipitating proteids suggested to Allen and Searle[2] the use of bromine. They reported that bromine quantitatively precipitates the products formed by the peptic digestion of egg-albumin, and they developed the method practically as given above. As applied to the separation of peptones from amido acid compounds in cheese and milk, the method gives varying results, depending upon the age of the cheese or milk used.

In the case of our water extracts made from cheese nine months to a year old, crystalline bodies in noticeable quantities are precipitated by bromine along with peptones, due

[1] Analyst, **22**, 226 (1897).
[2] *Ibid.*, **22**, 259 (1897).

probably to the presence of tyrosine, giving the solution a turbid appearance and rendering filtration difficult. Schjerning[1] has shown that tyrosine behaves in this manner with bromine water. This precipitate is partly retained on the filter-paper and is estimated as peptone.

Schjerning has shown also that bromine does not completely precipitate milk proteids and their derived caseoses and peptones. Of the whole proteid, he obtained only 76.7 per cent by bromine. In the case of milk, we have obtained results varying with the age of the milk. In perfectly fresh milk, when the amount of amido compounds must have been least, we obtained 91.3 per cent of the entire milk proteids by bromine precipitation. In another case of fresh milk we compared the precipitation of proteids by bromine and hydrochloric acid with that by tannin and sodium chloride, and by phosphotungstic acid solution and sulphuric acid, with the following results:

Precipitated by	Per cent of total nitrogen.
Phosphotungstic and sulphuric acids	93.8
Tannin and sodium chloride	93.3
Bromine and hydrochloric acid	91.5

There is also a possible source of error in connection with the use of bromine in precipitating peptones, when the filtrate from the bromine precipitate is used directly for the determination of amido acid compounds. We have found in the case of water extracts from cheese over one year old that there is an actual loss of nitrogen when bromine is allowed to stand in contact with the water extract. In the case of one cheese two years old, the cheese extract, consisting of caseoses, peptones, and amido acid compounds, contained nitrogen equivalent to 3.74 per cent of the cheese before adding bromine, while, after standing one hour in contact with bromine in hydrochloric acid solution, there remained only 1.52 per cent of nitrogen. In other words, there had disappeared 44.6 per cent of the nitrogen present before the addition of bromine. In cheese one year old we have found the loss varying from

[1] Ztschr. anal. Chem., **39**, 545 (1900).

nothing, in one case, to over 5 per cent in others. To show whether or not this loss came from the action of bromine on the caseoses or peptones, we removed the caseoses with zinc sulphate and, in another sample of cheese extract, we removed the caseoses and peptones with phosphotungstic acid, and the loss still occurred. By passing a current of air through the above extract in contact with bromine, and then through potassium hydroxide and through sulphuric acid, these reagents were found free from nitrogen compounds, indicating that the lost nitrogen disappeared in the form of free nitrogen, and not in the form of ammonia or nitrogen oxides. We cannot regard the method of determining the amount of peptones in cheese extracts by means of bromine as a reliable method, because, first, bromine precipitates small amounts of tyrosine and perhaps certain other similar compounds; second, it is not a complete precipitant of caseoses and peptones; and, third, its filtrate cannot be used for the determination of amido acid compounds, especially in old cheeses, owing to the decomposing effect of bromine upon such compounds, setting nitrogen free. In addition, bromine is a most disagreeable reagent to handle.

(4) *Comparative Value of Different Reagents Used in Separating Peptones and Amido Acid Compounds.*—We have now considered in some detail each of the three agents most commonly used in separating peptones from amido acid compounds, *viz.*: (1) Tannin-salt solution, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. Tannin and salt solution fails as a perfect reagent for the separation, because it does not completely precipitate peptones, which results in making the quantitative results for amido acid compounds too high, and may indicate the presence of considerable quantities of amido acid compounds even when they are practically absent. Phosphotungstic acid, on the other hand, completely precipitates peptones, but also precipitates some of the amido acid compounds that are present in cheese and milk, and the consequence is that the amount of amido acid compounds found is too low. Bromine is open to both

objections,—it fails to precipitate peptones completely, and at the same time does precipitate some of the amido acid compounds. While these two sources of error might tend to offset each other under certain conditions, we cannot depend upon such a method for reliable quantitative results.

In our judgment it is desirable, for best results, to use phosphotungstic acid to separate peptones and amido acid compounds, when the amount of the latter is relatively small as compared with peptones, or when they consist mostly of monoamido compounds. This condition occurs in the early stages of cheese ripening and persists longer in cheese cured at low temperatures. It occurs also in milk and cheese acted upon by pepsin enzymes, especially in the presence of chloroform.

Tannin-salt solution can be relied upon to give better results than phosphotungstic acid, when amido acid compounds are present in proportions that are relatively large compared with peptones, or when they consist largely of diamido compounds. The former condition prevails in normal cheese cured under usual conditions, especially after the first few weeks of curing.

10. *Determination of Nitrogen in the Form of Ammonia.*

We distil with magnesium oxide 100 cc. of the filtrate from the tannin-salt precipitation, passing the distillate into a standardized acid, and titrating in the usual way. In our early work the cheese mass itself, suspended in water, was used for distillation, giving slightly higher results than the method just described. The small increase is generally accounted for as coming from the proteids themselves present in the solution. Theoretically, it is true that when such bases as putrescine and cadaverine are present, they might distil with the ammonia. In one case where a large quantity of cheese was subjected directly to distillation with magnesium oxide and the distillate examined for these bases, none was found, the distillate containing only ammonia. The high boiling-points of cadaverine and putrescine, and the consequent difficulty of distilling them with steam probably accounts for their absence in the distillate.

In our early work on the determination of ammonia in milk and cheese, we subjected to distillation with magnesium oxide and with barium carbonate many different amido compounds, in order to ascertain if any of these bodies, when pure, could split off basic nitrogen. While some of the products used in our work are not at all likely to be found in cheese or milk, we include them with the others in the table given below. The method was carried out as follows: We dissolved 1 gram of each amido body, or, if insoluble, suspended it in 50 cc. of water, and, for distillation, used 10 cc. of this mixture diluted to 150 cc., adding magnesium oxide or barium carbonate and using ordinary atmospheric pressure.

Table III.—Effect of Distilling Amido Bodies with Magnesium Oxide and with Barium Carbonate.

	Amount distilled with magnesium oxide.	Amount distilled with barium carbonate.
Acetamide	0	0
Allantoin	0	0
Arginine[1]	0	0
Aspartic acid	0	0
Creatine	0	0
Creatinine	0	0
Diphenylamine	0	0
Glutamic acid	0	0
Glycocoll	0	0
Histidine	0	0
Leucine	0	0
Lysine	0	0
Phenylenediamine	0	0
Trimethylamine	completely distilled	completely distilled
Tyrosine	0	0
Uric acid	0	0
Xanthine	0	0

We have also used the excellent Nencki apparatus, distilling under reduced pressure the filtrate from the tannin-salt precipitation. In comparative trials we have obtained no lower results than when we distil under ordinary atmospheric pressure.

[1] Ztschr. physiol. Chem., 34, 145 (1901).

11. *Determination of Nitrogen in the Form of Unsaturated Paracasein Lactate.*

The residue insoluble in water is treated with several portions of a 5 per cent solution of sodium chloride, the process being carried out as in preparing the water extract in 3, above. The nitrogen in an aliquot part of the 500 cc. of this salt extract is determined by the Kjeldahl method.

II. METHODS FOR THE SEPARATION AND ESTIMATION OF THE NITROGEN COMPOUNDS OF MILK AND THEIR PROTEOLYTIC PRODUCTS.

We will briefly describe the methods used for the separation and estimation of the nitrogen compounds of milk and their proteolytic products in order.

1. *Determination of Total Nitrogen in Milk.*

Weigh about 5 grams of milk and determine the nitrogen by the Kjeldahl method.

2. *Determination of Casein.*

To about 10 grams of milk add 90 cc. of water at 40° to 42° C., and then 1.5 cc. of 10 per cent acetic acid. Agitate and warm at the temperature given above until a flocculent precipitate separates, leaving a clear supernatant liquid. Filter, wash, and treat by the Kjeldahl method for estimating nitrogen.

In fresh milk, 2 or 3 cc. of a saturated solution of alum may be used in place of acetic acid, usually with little higher results. But when the milk-casein has been proteolyzed to any extent the use of alum is not permissible, since it precipitates caseoses in addition to casein.

The use of acetic or any other acid in precipitating casein in milk, whose casein has been digested in any degree, precipitates, in addition to casein, any paranuclein that is present. We have not yet succeeded in devising satisfactory methods for the separation of these two compounds.

3. *Determination of Nitrogen in the Form of Albumin and Syntonin.*

The filtrate from 2 is neutralized by caustic alkali, using phenolphthalein as indicator, and is then heated at the temperature of boiling water until the precipitate completely separates and settles. The precipitate is then filtered, washed, and treated by the Kjeldahl method.

4. *Determination of Nitrogen in the Form of Caseoses.*

The filtrate from 3 we heat to 70° C., add 1 cc. of 50 per cent sulphuric acid, and then pure zinc sulphate to saturation. Let stand at the temperature indicated until the caseoses completely separate and settle. Then cool the mixture, filter, wash with a saturated solution of zinc sulphate made slightly acid with sulphuric acid, and treat the precipitate by the Kjeldahl method.

5. *Determination of Nitrogen in the Form of Amido Acid Compounds.*

Treat about 50 grams of milk with a tannin-salt solution or with phosphotungstic acid according to directions given under 8, page 157.

6. *Determination of Nitrogen in the Form of Peptones.*

From the total nitrogen subtract that found in all forms other than that of peptones, as indicated under 9, page 157.

7. *Determination of Nitrogen in the Form of Ammonia.*

See under 10, page 167.

III. DETERMINATION OF CHLOROFORM.

When chloroform is used as an antiseptic in milk and cheese, it is very essential to know approximately the amount present in order that we may have proper control of the conditions. We have used the following method successfully: We place 5 grams of milk or cheese in a pressure-bottle with about 100 cc. of alcohol and 5 grams of caustic potash. The bottle is then heated in an autoclave for half an hour at 110° C. The resulting chloride is determined by titration as for chlorine in sodium chloride.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XLII.—AN APPARATUS FOR CONTINUOUS VACUUM DISTILLATION.[1]

By Charles F. Mabery.

The occasional contributions to methods for vacuum distillation seem to indicate that a method is still wanting that shall combine convenience and efficiency. It is quite true that the various attachments that have been suggested and that are described in dealers' catalogues fall short of efficiency in essential details. In the great amount of vacuum distillation carried on in this laboratory during the last fifteen years, probably much exceeding what has been done elsewhere in a single line of work, a durable apparatus has been gradually evolved in which this work can be carried on as expeditiously as distillations under ordinary pressures.

One of the most essential features is a regulator to maintain a constant tension, and the stop-cock G with lever attachment formerly described[2] and constantly in use is very satisfactory.

The chief features to be provided for in a convenient apparatus are the following :

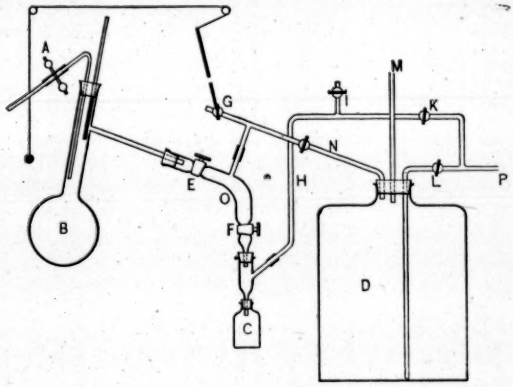
1. Exclusion of air from hot oil in still during change of receiver.
2. Admission of distillates into still without interruption.
3. Admission of air into receiver before removal of each fraction.
4. Exhaustion of receiver for new fraction without connection with still.

The complete apparatus in the form used at present is shown in the figure on the next page.

The fractions are drawn into the still through the tube closed by the nipper tap A. The still is exhausted by the tube N connecting the tube O with the vacuum reservoir D. The reservoir C is exhausted by the tube H, which connects with the water-pump through the tube P. Air is let into the receiver C by means of the cock I, and kept from the still by

[1] This method is a part of the work that is carried on in this laboratory with aid granted by the Academy of Arts and Sciences from the C. M. Warren fund for chemical research.

[2] Proc. Am. Acad., 31, 10.



the cocks E and F. The tube with the stop-cocks E and F affords a convenient means for separating fractions without interruption, and without admission of air into the still. The tube M leads to the manometer. By means of a single efficient water-pump the entire apparatus may be kept under a tension of 12 mm. or less during continuous distillation. By means of common corks, the apparatus is readily set up and easily kept tight by the use of rubber lute.

The tubes H and N may be given less rigidity by putting them together in sections with connectors. Any water that may occasionally run back from the pump is readily drawn out if the pipe P extends to the bottom of the reservoir D.

The apparatus in this form is especially adapted for the separation of fractions with high boiling-points. For very high temperatures the still must be packed in asbestos. For more volatile distillates a condenser should be inserted between the still and tube O, best by passing the exit tube of the still through the condenser. Our distillation flasks are made with a high exit tube to give a long neck, which is filled with broken glass resting on a piece of glass rod with a head, as previously described. As is evident from the figure, this

apparatus may be readily set up from supplies always at hand in the laboratory, except the tube O, which any glass-blower can make.

Suggestions as to details have been made by various assistants, especially by Mr. O. J. Sieplein, instructor in chemistry, who prepared the drawing.

NEW OSMOTIC MEMBRANES PREPARED BY THE ELECTROLYTIC PROCESS.

[PRELIMINARY ANNOUNCEMENT.]

By H. N. Morse.

The electrolytic method[1] is well adapted to the deposition, upon or within porous walls, of nearly every kind of precipitate which can be formed from electrolytes in solution. It affords, therefore, a ready means of ascertaining which of these possess the character of semipermeable membranes.

In view of the reasonable prospect that some of the membranes discoverable in this way will be found to have certain advantages over copper ferrocyanide, especially for the investigation of the osmotic pressure of particular classes of compounds, the author and others in this laboratory have undertaken to test in a systematic manner a large number of electrolytically deposited substances.

It is already apparent, as was probably to be expected, that the number of compounds which are capable of exhibiting the semipermeable character is very large. Of the substances thus far tested, the following have been found to manifest osmotic activity to a promising degree: the ferrocyanides of zinc,[2] cadmium, manganese, and uranyl; the phosphates of copper and uranyl; and ferric and aluminium hydroxides.

Up to the present time we have concerned ourselves exclusively with the question whether the substances under examination are active or not, and consequently have tested the compounds mentioned above with open manometers only. We are, therefore, not yet prepared to give any opinion as to

[1] This Journal, **26**, 80; **28**, 1.

[2] Tamman: Wied. Ann., **34**, 299 (1888).

how any one of them will behave under high pressure. But after having extended our search for semipermeable membranes as far as seems expedient, we shall proceed to subject those which offer the greatest promise of usefulness to a more careful study.

JOHNS HOPKINS UNIVERSITY,
Dec. 26, 1902.

OBITUARY.

JOHANNES WISLICENUS.

Professor Johannes Wislicenus, of the University of Leipzig, well known from his work in organic chemistry, especially that upon geometrical isomerism among organic compounds, died on the 5th of December, 1902. He was born in Klein-Eichstädt, near Querfurt, on the 24th of June, 1835, and was the oldest of a number of children. His father, Gustav Adolf Wislicenus, was a man of pronounced ability and marked independence in thought and action. On account of his connection with the *Burschenschaft*, in 1824, and while still a youth, the elder Wislicenus was sentenced to twelve years imprisonment, but was released in 1829. He then fitted himself for the ministry and was subsequently pastor of churches at Klein-Eichstädt and at Halle. He soon, however, attracted notice on account of the liberality of his utterances upon religious topics, and, in 1846, he was deprived of his pastorate because of his lack of accord with the authorities. He subsequently became pastor of a liberal church (*freie Gemeinde*) at Halle, but, in 1853, upon the appearance of his treatise entitled "Die Bibel im Lichte der Bildung unserer Zeit," he was again condemned to two years imprisonment. He succeeded, however, in escaping with his family and came to Boston, Mass., where he associated himself with men of corresponding liberality of views. He subsequently removed to Hoboken, N. J., where he started a school, but in 1856 he returned to Europe, making his home at Zürich.

The facts regarding the elder Wislicenus here outlined are significant as explaining how it came about that Johannes Wislicenus spent three years in the United States, and as showing the religious persecution which caused both father and son to separate themselves from church organizations as such. In accordance with the wishes of Professor Wislicenus, the recent funeral services were conducted in the chemical

lecture room of the University and, so far as can be judged from available reports, by his colleague, Professor Ostwald.

Wislicenus had, before coming to Boston, taken up the study of mathematics and the natural sciences at Halle, and had served as assistant in the chemical laboratory there. During his stay in Boston he became assistant to Professor Horsford, at Cambridge, and upon his return with his father to Hoboken he conducted, for nearly two years, a general analytical practice, having a laboratory at Hoboken and traveling about the country. He also lectured at the Mechanics' Institute in New York. It is interesting to note that at this time he, like his father, interested himself in public affairs and spoke eloquently in favor of abolition principles.

Upon his return to Europe he resumed his study of chemistry at Zürich and was afterward again assistant at Halle, but soon qualified as *Privat-docent* at the university at Zürich. About 1860 he was made professor at the university, and was transferred to the polytechnic school in 1870. In 1871 he was made director of the entire school. In 1872 he accepted a call to the university at Würzburg, and in 1885 was called to the University of Leipzig.

Professor Wislicenus devoted himself almost exclusively to research in the domain of organic chemistry. His contributions to chemical science are extensive, and from the beginning his published work deals largely with the development of theoretical conceptions concerning the character of organic compounds and their interactions. Among the first of these is a monograph entitled "*Theorie der gemischten Typen*," published about 1859. He afterward took an active share in the development of the modern views regarding valence and of the relation of the atoms as individuals to the structure of organic compounds. His name will, however, undoubtedly be most generally identified with the development of the conceptions of geometric isomerism among organic compounds and the methods for the study of this phenomenon.

The theory propounded nearly simultaneously by Le Bel and van 't Hoff that the optical activity of organic compounds was connected directly with the presence in the compound of one or more asymmetric carbon atoms, while it drew attention to the significance of the geometrical arrangement of the atoms within the space dominated by the molecule, remained comparatively unfruitful until about 1887. Wislicenus then published his monograph, "*Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren, ungesättigten Verbindungen*," in which he developed the application of the principle of geometric isom-

erism, and offered it as an explanation of the existence of such isomers as fumaric and maleic acids, tiglic and angelic acids, and crotonic and isocrotonic acids, for which no previous explanation had been found. From that date Wislicenus and his pupils accumulated a large amount of material in support of the Le Bel and van 't Hoff theory and his own development of it. This cannot be outlined here, but it may be said that the value of his contributions to chemical science lies not only in the accumulation of facts which are recorded as the result of his researches and those of his students, but in the incentive which his work has afforded to others for thought and investigation. In this connection his demonstration of the extensive use which can be made of acetoacetic ether and its derivatives in organic syntheses also deserves special mention.

Of the personality of Professor Wislicenus one can speak only with enthusiasm. Of large frame, with a magnificent head (the beauty of which in his later years was emphasized by a mass of snow-white hair and a heavy white beard), with a countenance of unusual intellectuality and kindliness, and with a full, sonorous voice, he represented a splendid type of manhood. In his lectures he spoke without notes, with great ease, and in language which, without being in any degree florid, was so full of well-rounded sentences that the effect produced upon the listener was akin to that produced by a musician whose every tone is so certainly true as to cause only a feeling of contentment and keen pleasure in his auditors.

The frank and kindly countenance was an index of the nature behind it. He had a complete abhorrence of all display and of the use of official titles which have little or no real significance. He was a warm friend, as well as an inspiring teacher, to all his pupils, and to many of them the knowledge that the last few years of his life have brought much pain and suffering has already been a source of regret. The news of his death will intensify this sorrow, while it will also recall many pleasant memories of a man whom it is good to have known and been able to count as a friend, and to whom chemical science will ever owe a debt of gratitude.

H. P. T.

REVIEWS.

RESEARCHES ON CELLULOSE. 1895–1900. By CROSS and BEVAN. New York: Longmans, Green & Co. 1901.

"This volume, which is intended as a supplement to the

work we published in 1895, gives a brief account of researches which have been subsequently published, as well as of certain of our own investigations, the results of which are now for the first time recorded." The authors refer to the book entitled "Cellulose," which was reviewed in a former number of this JOURNAL.[1] The greater part of the present work is taken up with abstracts of the original articles, as the material is of too varied a nature to permit of a continuous or connected treatment. The authors point out the immense importance of these researches and show that the carbohydrate industry is of more importance than the coal-tar industry, and urge greater activity on the part of English chemists in this direction. The book is printed on standard printing paper, made according to the specifications of the Society of Arts Commission, appointed to study the quality of papers both in relation to their several applications, and more especially for documents of permanent value. J. E. G.

WATER SUPPLY (Considered Principally from a Sanitary Standpoint). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. Third edition,[2] rewritten. New York: John Wiley & Sons. 1902. 8vo. vi + 448 pp. 40 figures and 22 half-tone plates. Cloth, Price $4.00.

Chemists and all others having to deal with water supplies will cordially welcome this new and practically rewritten edition of Professor Mason's standard work on "Water Supply." In the present edition of the book, which is the third, the treatment of the following subjects deserves especial mention: The mosquito-malarial theory and the experiments of Celli and Manson touching upon the transmission of malaria; The relation between the growth and decay of algæ and the resulting odors observed in waters, particularly those of lakes and reservoirs; The relation of goitre to drinking water, and Kocher's investigations thereupon; and Alessi's experiments as to the production of artificial typhoid in animals. Under the head of filtration, the author discusses the workings of the new filtering plants at both Albany and Ashland, together with statistics illustrating the influence of such filtration upon the death-rates due to typhoid. Much new material has been added under the subject of mechanical filtration, including a discussion of the new iron coagulant. Space is given to the consideration of the merits of the rival systems of filtration, American and English, and to the question of properly choosing between them for municipal filtra-

[1] This JOURNAL, 17, 622.

[2] The first edition of this book was reviewed by Prof. Mallet, of the University of Virginia, in this JOURNAL, 18, 625 (1896).

tion. Under the title Self-purification of Streams the recent investigations concerning the pollution of the Illinois river by the opening of the Chicago drainage-canal are given and commented upon. The question of the purification of water by freezing, and the important question of the contamination of ice supplies are both fully covered.

A point of particular importance is touched upon in showing the tendency of dissolved gases, such as oxygen and carbon dioxide, to attack iron at boiler temperature.

All the statistical tables are brought up to date and the book is provided with an excellent index. The chapters upon the Chemical and Bacteriological Examination of Water have been omitted from the present edition, for the reason that they have been published separately in book form for the more convenient use of students. W. R. O.

A MANUAL OF VOLUMETRIC ANALYSIS. Treating on the subjects of Indicators, Test-papers, Alkalimetry, Acidimetry, Analysis by Oxidation and Reduction, Iodometry, Assay Processes for Drugs with the Titrimetric Estimation of Alkaloids, Estimation of Phenol, Sugars, Tables of Atomic and Molecular Weights. By VIRGIL COBLENTZ, PH.D., PHARM.M., F.C.S., Professor of Chemistry in the New York College of Pharmacy. Philadelphia: P. Blakiston's Son & Co. 1901. Price, $1.25 net.

"This manual is intended to serve as a systematic introduction to the principles of volumetric analysis based on modern theories. Especial attention has been devoted to the theory of ionization and its application to indicators."

This work is especially designed for the student of pharmacy and medicine, and is written in such a clear, logical manner that these students can gain a good idea of the principles involved, even in the short period which they generally have at their disposal.

The value of this book is further enhanced by the introduction in each case of a detailed description of the methods of calculation and of practical examples. A general idea of the field covered in this work can be obtained from the title.

J. E. G.